POLYVINYL ALCOHOL SIZE RECOVERY AND REUSE VIA VACUUM FLASH EVAPORATION

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Kishor Kumar Gupta

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POLYVINYL ALCOHOL SIZE RECOVERY AND REUSE VIA VACUUM FLASH EVAPORATION

Approved by:

Dr. Fred L. Cook, Advisor
School of Polymer, Textile and Fiber Engineering
Georgia Institute of Technology

Dr. John D. Muzzy
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

Dr. Wallace W. Carr
School of Polymer, Textile and Fiber Engineering
Georgia Institute of Technology

Dr. Radhakrishnaiah Parachuru
School of Polymer, Textile and Fiber Engineering
Georgia Institute of Technology

Dr. Matthew J. Realff
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology

Date Approved: April 2, 2009

To the everlasting affection and support of

my mom, dad,

my wife Preeti,

my daughter Arulita and son Anirudhha

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LIST OF SYMBOLS

A	Horizontal cross-sectional area of flash chamber [m^2]
c_p	Specific heat of liquid [J/kg K]
H	Height of liquid [m]
h_{fg}	Latent heat of vaporization [J/kg]
m_{ev}	Evaporated mass of liquid [kg]
$\dot{m}_{ev}$	Instantaneous evaporated mass flow [kg/s]
T_o	Initial temperature of water [^oC]
ρ1	Density of liquid [kg/m3]
h_{fg}	Latent heat of vaporization [J/kg]
m	Mass of liquid [kg]
T	Temperature of water [^oC]
Δm	Change in mass [kg]
dT	Change in temperature [^oC]
W	Wet yarn weight / length
D	Dry yarn weight / length
S	Slashed solution concentration
t	Flow time of solution
c	Concentration of the solution
η_{red}	Reduced viscosity
η_{sp}	Specific viscosity
η_{red}	Reduced viscosity

η_r	Relative viscosity,
$[\eta]$	Intrinsic viscosity
k_H	Huggins constant
η_{inh}	Inherent viscosity
k_A	Kraemer constant
K, α	M H constants
M	Viscosity-average molecular weight
m	Slope of the line
b	Intercept on y axis
c	Concentration

LIST OF ABBREVIATIONS

VFE Vacuum flash evaporation

UF Ultrafiltration

PVA Polyvinyl alcohol

COD Chemical oxygen demand

POTW Primary oxygenation treatment of water

UGA University of Georgia

ROI Return on investment

BOD Biological oxygen demand

MW Molecular weight

SUMMARY

Polyvinyl alcohol (PVA) desize effluent is a major Chemical Oxygen Demand (COD) contributor to a textile plant's Primary Oxygenation Treatment of Water (POTW) operation, and being biologically inert, it presents a threat to the environment. Unfortunately, no effective and efficient means to treat PVA desize effluent has been implemented in the textile industry. Ultrafiltration (UF) reverse osmosis technology for the recovery and recycling of PVA size is more than 35 years old, but it is not used widely because of its many disadvantages. The situation necessitates a new technology for the recovery and recycling of PVA size which can reduce energy and water consumption in an economical and environmentally-friendly manner.

A new technology that would eliminate the disadvantages of the current ultrafiltration process in the recovery of PVA from desize effluent is vacuum flash evaporation (VFE). The VFE process for recovery and concentration has been used in a variety of other industries, but has never been demonstrated for size recovery in the textile industry.

The reported research is concerned with the VFE process and its economics, and the properties/utilization of the recovered PVA emanating from the process. This research was divided into four parts. In the first and second parts, simulated, recycled PVA size formulations at different impurities concentration were prepared with or without wax, films were made and yarns were slashed to determine their changes in properties as a function of cotton chemical impurities concentraion from 0% to 100%. In the third part and building on the bench scale results, the slashing process was optimized and the

concept was demonstrated using the University of Georgia (UGA) Webtex® Pilot Slasher. In this demonstration, both ground and pile yarns of a common residential towel construction were slashed, with one conventional cycle followed by five size recovery/recycle slashings. The last part involved the economical feasibility of the VFE technology in recovery and recycling of PVA size.

With VFE recovery, recycled size was found to contain extracted cotton chemical impurities which decreased the apparent molecular weight of the recycled PVA size, as they (fatty acids, alcohols, waxes, etc.) were of low molecular weight, thus decreasing the breaking strength of the recycled size film. The initial studies were conducted without the addition of wax to the size. In conventional slashing with wax added to the PVA, film strength also decreased. With the occluded cotton impurities present in the recycled PVA film, no wax was required to be added to the recovered size, as the impurities performed the same film physical property modifications as the wax.

An increase in elongation at break of recycled PVA film can render weaving processes more efficient. Mostly cotton is used in the towel industry, but 100% PVA size without substantial added wax (~8%) cannot be used to slash the pile yarns of the construction because PVA slashed yarn is stiff in nature, making it difficult to form the loops. However, the recovered PVA size from the developed VFE process showed a decrease in bending length, facilitating the use of PVA size in the towel industry.

As recovered PVA was added along with virgin PVA in the size box, the cotton yarn chemical impurity levels continued to increase and reached a steady state after ~five slashing cycles in a size recovery/reuse sequence. At constant solids concentration, viscosity decreased with the number of size recycles, which aided size yarn penetration at

the application temperature (70^{o}C). A small increase and then decrease in slashed yarn load at break occurred with impurities concentration increase in the film; however, slashed yarn load-at-break was always more than 20% that of un-slashed yarn. Slashed yarn elongation at break initially increased then decreased with recycling, but it was always more than or close to that of un-slashed yarn. Slashed yarn hairiness remained nearly constant with recycling. Slashed yarn abrasion cycles to first yarn break initially increased, but remained nearly constant on further recycling. Desized yarn color was also constant with recycling. The overall research results quantified an improvement in recycled size slashed yarn properties over those of greige yarn for towel weaving.

Size must be removed from fabric after weaving in a desizing operation (part of the preparation wet process) to facilitate subsequent dyeing and finishing. The recycled size film was easy to wet, which aided the desizing of slashed yarns.

Based on the pilot scale trial results, comparative economics were developed for model towel manufacturing plant implementation of the VFE concentration technology for all-PVA size towel weaving, implementation of the analogous UF concentration technology, and the current PVA/starch/wax blend size process with no material/water recovery. Incorporation of the VFE technology for PVA size recovery and recycling resulted in ~$3.2M/year in operational savings over the conventional PVA/starch/wax process with no size recycling, yielding a raw return on investment (ROI) of less than one year, based on a $3M turnkey capital investment [1].

The results confirmed that VFE can be successfully implemented to recover and reuse PVA size, not only by developed nations, but also by the growing economies like China and India which are hesitant to use the present technology of UF due to its clear

disadvantages and operating cost ineffectiveness. Widespread use of VFE to recover and reuse PVA size will aid in minimizing water pollution and chemical, energy and water consumptions in the global textile industry, thereby contributing to a greener, cleaner world.

CHAPTER 1

INTRODUCTION

The world is facing the gigantic task of meeting its ever-rising energy and potable water requirements while reducing pollution loads. World energy demand is expected to increase from 447 quadrillion Btu in 2004 to 702 quadrillion Btu in 2030 [2]. In 2004, 94% of the total energy consumption came from non-renewable resources. The demand for petroleum is projected to increase by 40%, coal 74% and natural gas 62% by 2030 [2]. Unrestricted burning of fossil fuel will further contribute to the green house effect and global warming. One third of the world's population does not have enough potable water, and this fraction will increase to two thirds by 2025 [3]. The greatest challenge is to solve the crisis of exhausting non-renewable energy resources and increasing demand without affecting world development and growth. An urgent need exists to save energy, chemicals and water in industrial processes while reducing pollution loads at every front, either by developing new technologies or by innovative applications of existing technologies in different areas.

The textile industry is one of the oldest in history and provides a basic requirement of all human beings. Unfortunately, the industry is one of the most water consumptive and polluting, and a huge consumer of energy [4-7]. In the textile manufacturing process of slashing, yarn is coated with a polymeric size to improve its weaving properties [4]. Polyvinyl alcohol (PVA) and starch are the sizes that are widely used in the textile industry, often as a blend. After weaving, size is removed from the

fabrics in the preparation process of desizing. Voluminous hot water is utilized in desizing, and if both PVA and starch are present, the effluent is a high Biological Oxygen Demand (BOD)/Chemical Oxygen Demand (COD) contributor to the plant's Primary Oxygenation Treatment of Water (POTW) operation. Starch itself contributes 50% of BOD in composite textile effluents (100,000-600,000 mg L-1) [4, 8], whereas no known bacteria has yet evolved to generate enzymes that attack and degrade the synthetic PVA polymer backbone (PVA was invented only ~85 years ago) [9]. The desize pollution streams containing synthetic PVA are a threat to the environment [4-7], so textile plants have to carefully process the desize effluent sent to the POTW. The treatment of such large volumes of desize effluent is costly. When an all-PVA/wax size is used, significant incentives exist to recover the size material from the desize wash water stream, concentrate it and reuse it. Unfortunately, no effective and efficient means to do this has ever been implemented in the industry. Ultrafiltration (UF), operating on the principle of reverse osmosis and based on spiral-wound, polymeric membrane films, has been used for this purpose in the U. S. on a very limited basis, mainly where forced by regulatory authorities. However, this technique has not found widespread industrial acceptance because of high capital investment, high operating costs and poor effectiveness. Starch size is not appropriate for significant recovery and repeated reuse cycles because the natural material is subject to chemical/biological breakdown by starchase enzyme-producing bacteria with time, i.e., the formulation "sours" [4-7, 10].

In UF, the semi-permeable membrane excludes the high molecular weight PVA of the desize effluent stream, whereas low molecular weight PVA and water passes through the membrane. The hot permeate containing the low molecular weight tail of the PVA

distribution is sometimes re-used in “dirty” applications, e.g., as make-up water for wash boxes in preparation processes after scouring [11], whereas the recovered PVA is mixed with virgin PVA (usually in a 70:30 weight ratio) [11] and is reused in slashing. The UF process in recovery and recycling of PVA has the following limitations and disadvantages [5, 12]:

- The spiral wound polymeric membranes can foul, requiring process shutdown for cleaning, adding to operational costs. The membranes also degrade and decompose in use, requiring expensive, periodic replacements.

- A heavy pressure drop (up to 500 kPa) exists across the membranes, requiring high pumping pressures to force the water through the filters, leading to high electrical consumption.

- Loss of much of the low molecular weight (MW) “tail” from the PVA distribution contained in the desized stream which passes through the UF filter under the high pumping pressures (~3-5% of the total mass available). The contamination of the separated water stream with the low MW PVA results in added PVA costs and restricts the potential reuse of the exiting hot water in other textile processes in the plant, e.g., as dye bath make-up water because of the process interference factor presented by the PVA in, for example, pastel shade development.

A new technology that would eliminate the disadvantages of the current PVA UF recovery process is Vacuum Flash Evaporation (VFE). Some of the commercial uses of VFE evaporation include separating volatile matter from polymer solutions [13], water from crude 1,4-butanediol [14] and water from clay slurries [15]. The VFE process for recovery and concentration has been used in a variety of industries, but has never been

demonstrated for PVA size recovery in the textile industry. In this technology, the excess water in the dilute PVA desize stream is vacuum flash evaporated in a controlled pressure manner [16]. The steam that is produced from the VFE unit is condensed and utilized as hot, clean make-up water in any plant wet processes (dyeing, preparation, washing, etc.). The energy "penalty" incurred by installing a VFE unit and phase transforming water (~1000 Btu's/lb. of water) is thus minimized, as approximately the same energy used to concentrate the PVA size would be used anyway by the plant in the form of boiler feed energy to produce steam for heating water in the facility's existing wet processes. In addition, all of the water contained in the desize stream is recovered and recycled back into the plant, giving a true closed-loop character to the overall desizing-size concentration/reuse sequence of processes and aiding the overall process economics. In the reported case of PVA size recovery by VFE, the concentrated PVA stream exiting the VFE process also contains the low molecular weight "tail" of the PVA distribution that is currently lost in the UF process, and thus the former will have more favorable material balance economics than the latter. The reported thesis research investigated the VFE process and its economics in PVA size recovery/concentration, and the properties/utilization/performance of the recovered PVA emanating from the process.

In the VFE process, when abrupt pressure drops occur on a water surface, surplus heat in the liquid is transferred into latent heat of vaporization. Following Fick's Law of diffusion, the abrupt drop in pressure increases the mass flow rate 10-12 times more than that of simple thermal evaporation. A super cooled and super heated heterogeneous profile is developed on the liquid surface due to flash evaporation [16]. To make the process more efficient, the liquid is injected into the evaporator by a spray nozzle [17].

VFE can thus operate at lower temperatures to phase transform water from the liquid to the vapor phase, e.g., 30^{o}C [18]. At a low liquid temperature, high vacuum is required, whereas at a high temperature, low vacuum is needed [16]. The heat exchanger incorporated directly into the VFE unit works very efficiently. The VFE unit manufactured by VACOM LLC claims that up to 90% of the heating energy is recovered by the unit's heat exchanger [19]. As a result, the energy required to heat the incoming desize effluent stream at steady state is substantially lowered. The desize effluent stream available for flash evaporation is normally $\leq$ 90^{o}C in temperature. Because of its relatively high temperature, the vacuum required for flash evaporation of the stream is very low. Energy input into the VFE process is thus needed mainly for pumping water and operating vacuum pumps. VACOM, LLC reported that for its VFE equipment, the total energy costs for running a suitably-sized VFE unit for the selected model plant desize effluent volume/hour was an average of $0.006/feed gallon [1]. When processing desize water at ~90^{o}C, energy costs will thus be less than for a stream entering the VFE process at ambient temperature. First, low vacuum is needed because of the high temperature of the incoming desize effluent stream. Second, evaporation at higher temperature increases the mass flow rate.

One gallon of desize effluent contains 0.083 lb of PVA if the initial concentration of PVA is 1%, and this mass has a value of $0.08316, considering the virgin PVA cost at ~$1/lb [16]. If the desize effluent of a large operating plant is 100,000 gallons/day and the plant operates 350 days/year, the savings in recycled PVA alone would be $2.9M/year. VFE unit manufacturers claim that if the recovered material has some

inherent value, then the raw ROI of installing a plant-size unit for PVA concentration and recovery could be as little as a few months to a year [20].

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

2.1.1 Energy Consumption in the Textile Industry

Textile manufacturing is one of the oldest industries in history and serves a basic requirement of all human beings. The global textile industry is one of the largest consumers of energy [4-7]. The world's energy consumption per year required for desizing alone is more than the total annual household energy consumption of some countries [21, 22]. The world is facing the gigantic task of meeting its ever-increasing energy requirements. World energy demand is expected to increase from 447 quadrillion Btu in 2004 to 702 quadrillion Btu in 2030 [2]. In 2004, 94% of the total energy consumption came from non-renewable resources. The global demand for petroleum is projected to increase by 40%, coal 74% and natural gas 62% by 2030 [2]. Unrestricted burning of fossil fuels will further contribute to the green house effect and global warming. The greatest challenge is to solve the crisis of exhausting non-renewable resources and increasing demand without affecting global development and growth. An urgent need exists to save energy at every front, either by developing new technologies or by innovative applications of existing technologies in multiple arenas.

2.1.2 Slashing

Weaving is a process in which heddles move up and down and a reed moves forward and backward at high speed (Figure 2.1) [23]. Warp yarns undergo excessive stress, strain, abrasion, etc., due to these moving metal parts.

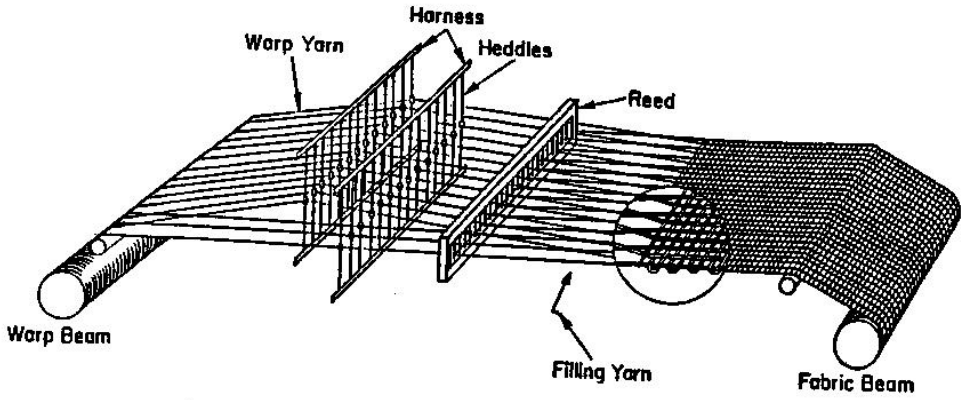

Figure 2.1: Heddles and Reed Positions in Weaving [23]

Greige warp yarns are weak, and they frequently break in modern high-speed weaving processes. In order to make the warp yarns more weave able, their properties (tensile strength, abrasion resistance, etc.) must be improved by a process known as slashing. In slashing, greige warp yarns are dipped in a polymeric size solution, squeezed between rollers to a predetermined pickup and then dried and the size film cured on steam drying cans. After slashing, yarns have a thin film of size on them with some size penetration (Figures 2.2-2.3). The purpose of slashing is to improve the warp yarns' weave ability by increasing their tensile strength, flexibility, abrasion resistance, etc. These properties help in improving weave ability, but they need to be optimized, because after certain critical points, continued increases in these properties actually decreases the

weave ability, e.g., a too-high increase in yarn tensile strength leads to a decrease in elongation at break.

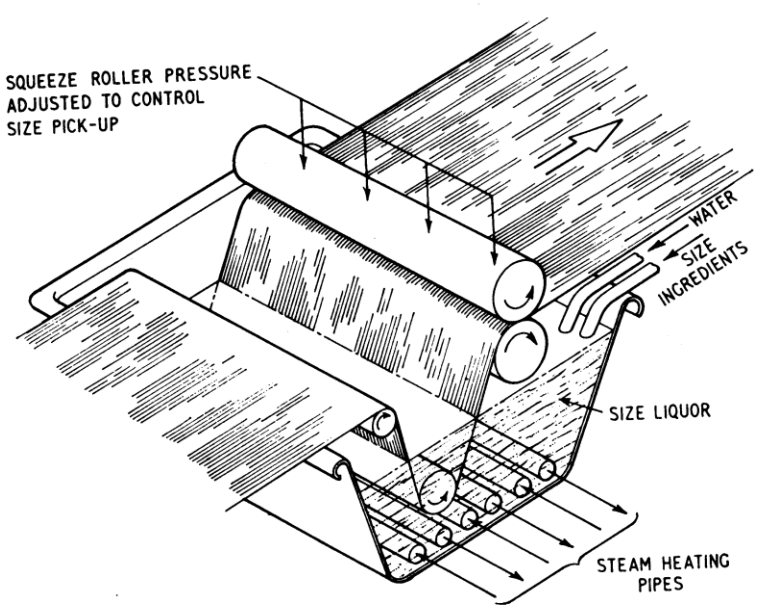

Figure 2.2: Section of Size Box [24]

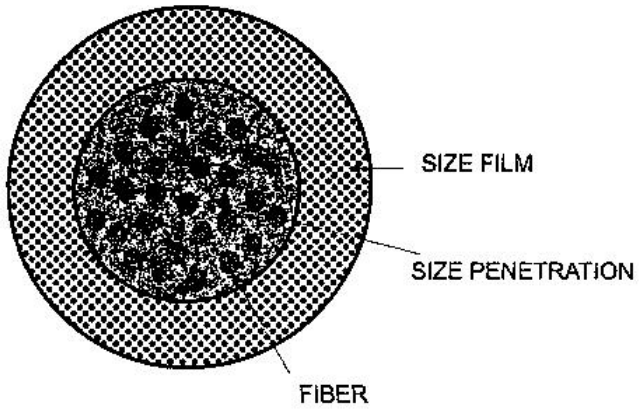

Figure 2.3: Fiber Size Binding in a Yarn [25]

An ideal size increases the strength of warp yarns by cementing the fibers in the structure and preventing fiber slippages [26], which leads to a corresponding decrease in elongation at break (the latter should not go below 20% of the corresponding greige yarn elongation at break) [25, 27].

Control of size penetration into the individual yarn diameter is needed as increased size penetration decreases flexibility and increases stiffness. Flexibility of the yarn is an important property because warp yarns bend under tension as heddles move up and down with the harnesses. Size film on slashed yarns may crack, leading to an increase in friction if the warp yarns are not flexible and causing warp yarn breakages in weaving. In towel weaving, if the pile slashed yarn is very stiff, it becomes difficult for the terry weaving machine to form the loop. Efficient slashing should create a uniform, smooth size film on the yarn, which will reduce friction and hold the surface fibers in place. The most common slashing agents are PVA and starch, most commonly in PVA-heavy blends of the two, e.g., 60:40 or 70:30 [28, 29]. Filling (weft) yarns in weaving are not slashed.

2.1.3 Desizing

Slashing is conducted to facilitate the weaving process. After weaving, the fabric needs to be desized to facilitate colorant/chemical uptake in subsequent wet processes, e.g., dyeing and printing. The desizing process is critically important for quality dyeing and printing. In desizing, applied size is removed from the woven cloth by passing it through wash boxes at high temperature. The temperature of the wash box and the number of wash boxes required in series are dependent upon the desizing process and type of cloth. Desize ability of the size is measured by considering two factors: the

percentage of size left in the fabric, and the concentration of the size in the desize effluent stream. Enzymes are most commonly employed for desizing of starch-slashed fabric. Enzyme desizing is performed at controlled temperature, pH and electrolytes. The PVA copolymer size Elvanol® T-66 utilized in this research can be removed up to 97% level using hot water alone at 95^{o}C [30]. E. I. DuPont Co. recommends using only hot water for Elvanol© T-66 PVA desizing if the size is to be recovered from the desize effluent stream and reused.

2.1.4 Pollution from Desizing

In the process of slashing, yarns are coated with a polymeric size that improves its weaving properties [4]. Polyvinyl alcohol (PVA) and starch are the sizes that are widely used in the textile industries, often as a blend. After weaving, size is removed from the fabrics in the preparation process of desizing. Voluminous hot water is utilized in desizing, and if both PVA and starch are present, the effluent is a high Biological Oxygen Demand (BOD)/Chemical Oxygen Demand (COD) contributor to the plant's Primary Oxygenation Treatment of Water (POTW) operation. Starch itself contributes 50% of BOD in composite textile effluents (100,000-600,000 mg L-1) [4, 8], whereas no known bacteria has yet evolved to generate enzymes that attack and degrade the synthetic PVA polymer backbone(PVA was invented only ~85 years ago) [9]. The desize pollution streams containing synthetic PVA are a threat to the environment [4-7], so textile plants have to carefully process the desize effluent sent to the POTW. There are four ways of separating size from desize effluent stream: biodegradation; bioelimination (adsorption by sludge); precipitation; and ultrafiltration (UF) [7, 31, 32]. Biodegradation is used for natural sizes, whereas the last three are used for synthetic sizes. The first three processes

produce copious quantities of sludge which requires disposal; however, in UF and VFE size concentration systems, the PVA is recovered and recycled with no sludge formation.

2.1.5 Size Recovery

The treatment of large volumes of desize effluent is costly. When an all-PVA/wax size is used, significant incentives exist to recover the size material from the desize wash water stream, concentrate it and reuse it. Unfortunately, no effective and efficient means to do this has ever been implemented in the industry. Ultrafiltration (UF), operating on the principle of reverse osmosis and based on spiral-wound, polymeric membrane films, has been used for this purpose in the U. S. on a very limited basis, mainly where forced by regulatory authorities. However, this technique has not found widespread industrial acceptance because of high capital investment, high operating costs and poor effectiveness. Starch size is not appropriate for significant recovery and repeated reuse cycles because the natural material is subject to chemical/biological breakdown by starchase enzyme-producing bacteria with time, i.e., the formulation "sours" [4-7, 10].

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- A heavy pressure drop (up to 500 kPa) exists across the membranes, requiring high pumping pressures to force the water through the filters, leading to high electrical consumption.

- Loss of much of the low molecular weight (MW) "tail" from the PVA distribution contained in the desized stream which passes through the UF filter under the high pumping pressures (~3-5% of the total mass available). The contamination of the separated water stream with the low MW PVA results in added PVA costs and restricts the potential reuse of the exiting hot water in other textile processes in the plant, e.g., as dye bath make-up water because of the process interference factor presented by the PVA in, for example, pastel shade development.

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by the unit's heat exchanger [19]. As a result, the energy required to heat the incoming desize effluent stream at steady state is substantially lowered. The desize effluent stream available for flash evaporation is normally $\leq 90^{o}C$ in temperature. Because of its relatively high temperature, the vacuum required for flash evaporation of the stream is very low. Energy input into the VFE process is thus needed mainly for pumping water and operating vacuum pumps.

2.1.6 Cotton Impurities

In the case of size recovery using UF, some cotton chemical impurities along with low molecular weight PVA pass through the membrane, whereas in VFE, they remain in the recovered size. Impurities in the cotton mainly depend upon the soil and climate of the region where it grows and the variety of the cotton. Peters and Trotman detailed the constituents of typical raw cotton fiber as: cellulose, 88.0-96.0% by weight; proteins, 1.1-1.9%; pectic substances, 0.7-1.2%; ash, 0.7-1.6%; waxes, 0.4-1.0%; maleic, citric and other organic acids, 0.5-1.0%; total sugars, 0.3%; and pigment traces and others, 0.9% [33, 34]. The cellulose weight percentage after scouring and bleaching of cotton fibers reaches as high as 99%.

2.2 Polyvinyl Alcohol

2.2.1 Introduction

PVA is one of the most commonly used sizes in today's market, and was first introduced into the textile industry in 1965. PVA can be used with or without other sizing agents, e.g. starch, polyester resin, CMC and acrylic size. PVA/starch blend sizes are most commonly used in slashing. The stronger PVA film provides better resistance to

warp yarns against abrasion in high speed weaving than does a pure starch film, while starch ameliorates the strength of the PVA film while reducing the cost of the overall size formulation [25].

2.2.2 PVA Homopolymer

PVA is manufactured from vinyl acetate monomer (VAc). VAc is the starting raw material for PVA, as the monomer vinyl alcohol does not exist in nature (spontaneously tautomerizes to the more-stable acetaldehyde). Manufacturing PVA from VAc is a two stage process as shown in Figure 2.4. First VAc is polymerized to polyvinyl acetate (PVAc), and the PVAc is then hydrolyzed with NaOH to PVA:

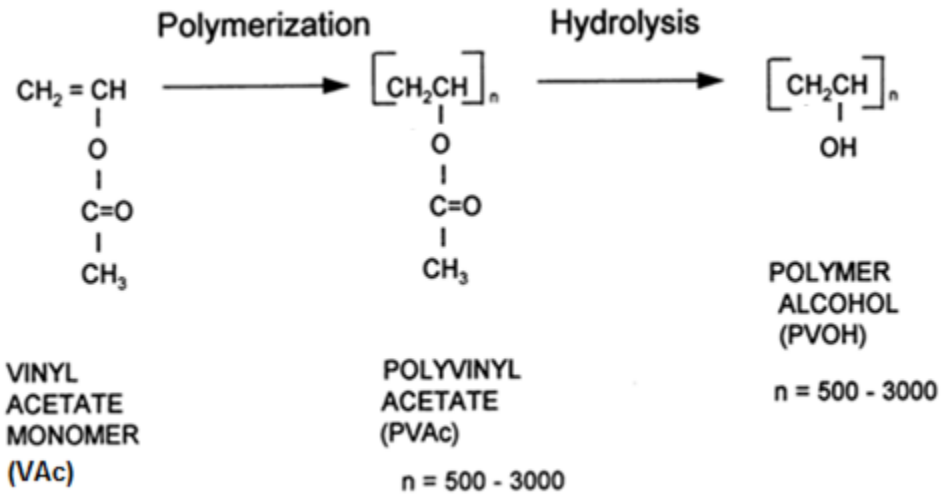


Figure 2.4: Chemistry of Polyvinyl Alcohol Manufacturing [35]

In the hydrolysis, acetate groups are largely replaced by alcohol groups (Figure 2.5), and the percentage of acetate groups replaced determines the degree of hydrolysis. If 86-88% of the acetate groups in the precursor PVAc are replaced by alcohol groups, the

material is called partially hydrolyzed. Similarly, if 95-97% of the groups are replaced, the material is referred to as intermediately hydrolyzed. Finally, if ≥98% of the acetate groups are converted, the product is called fully hydrolyzed.

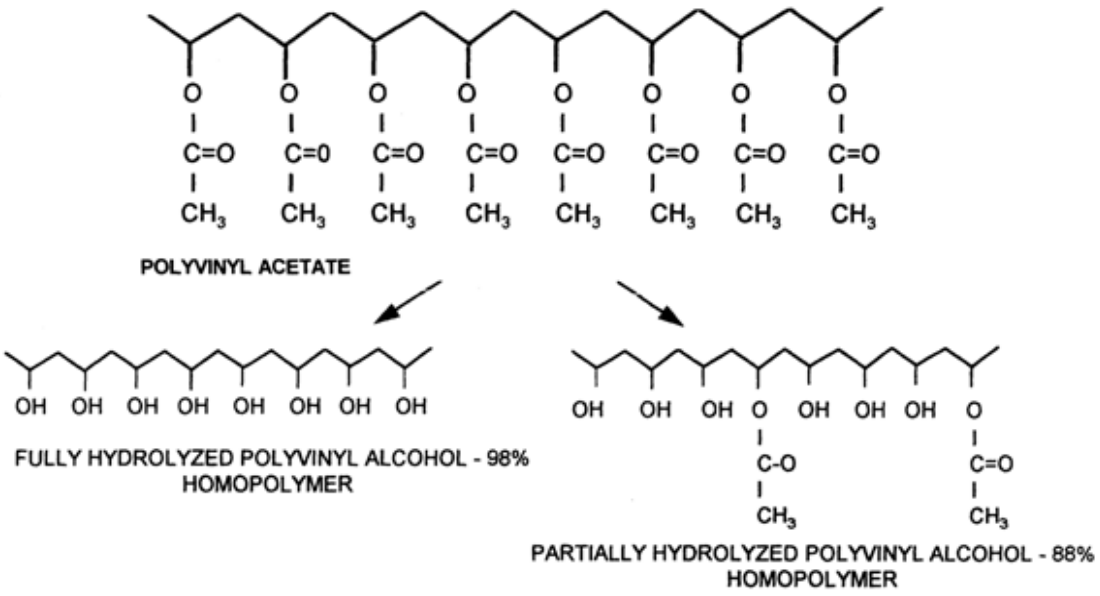


Figure 2.5: Hydrolysis of Polyvinyl Acetate to Polyvinyl Alcohol

2.2.3 PVA Copolymer

The PVA copolymer utilized in this research, E. I. Dupont Company's Elvanol® T-66, is formed by first polymerizing VAc and another comonomer (Figure 2.6). VAc and the proprietary comonomer are polymerized to corresponding PVAc copolymer, which is then hydrolyzed with NaOH to the PVA copolymer (Figure 2.7).

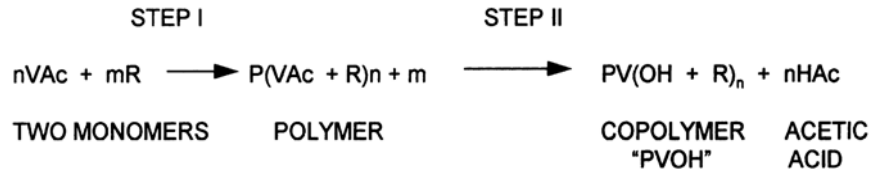


Figure 2.6: PVA Copolymer Manufacturing [35]

The comonomer employed is non-hydrolysable and makes the copolymer more stable to hydrolysis. The degree of hydrolysis of the copolymer is close to that of the PVAc homopolymer.

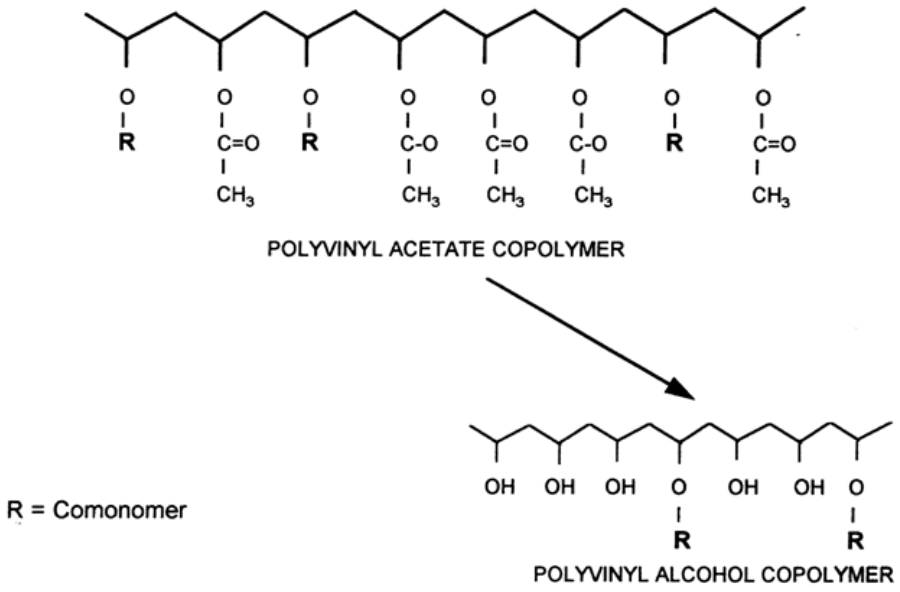


Figure 2.7: Hydrolysis of PVAc Copolymer to PVA Copolymer [35]

Some of the properties required by a PVA slashing agent include the following: compatible with other sizing agents; readily soluble in water; easily removed from the fabric in desizing; and should not be altered chemically by the concentration/recovery

process. PVA grades below 88% hydrolysis are not 100% soluble in hot water (~140°F, Figure 2.8), whereas all PVA grades above 88% hydrolysis are soluble.

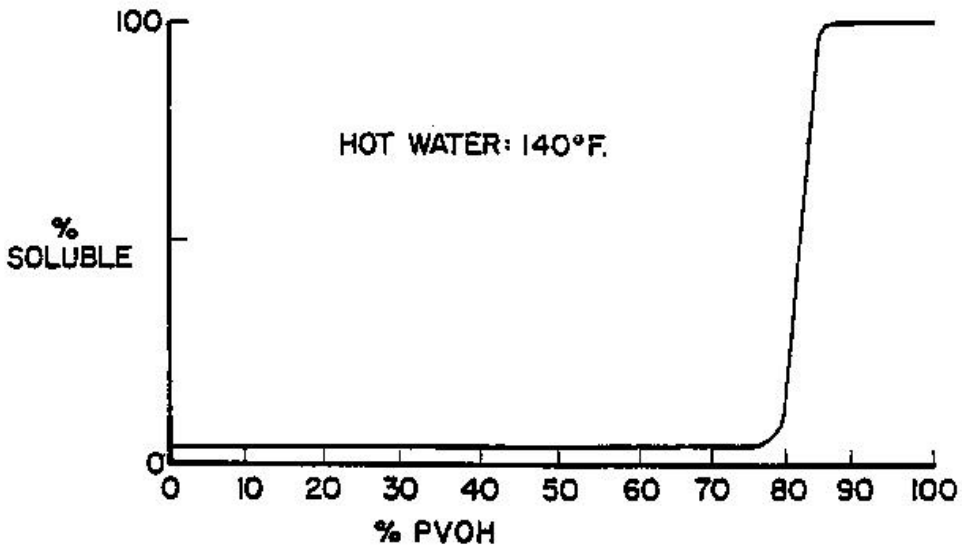


Figure 2.8: Water Solubility of PVA at 140°F [25]

PVA film becomes heat set during drying/curing on steam cans in the slashing process, causing a water solubility decrease and requiring a higher temperature to desize (Figure 2.9). The solubility rate of heat set PVA film can be increased by increasing the desize water temperature. Acceptable desizing for all grades of PVA slashed yarn can be achieved at temperatures from 170 –190°F, but DuPont Elvanol® T-66 PVA is easy to desize (Figure 2.10).

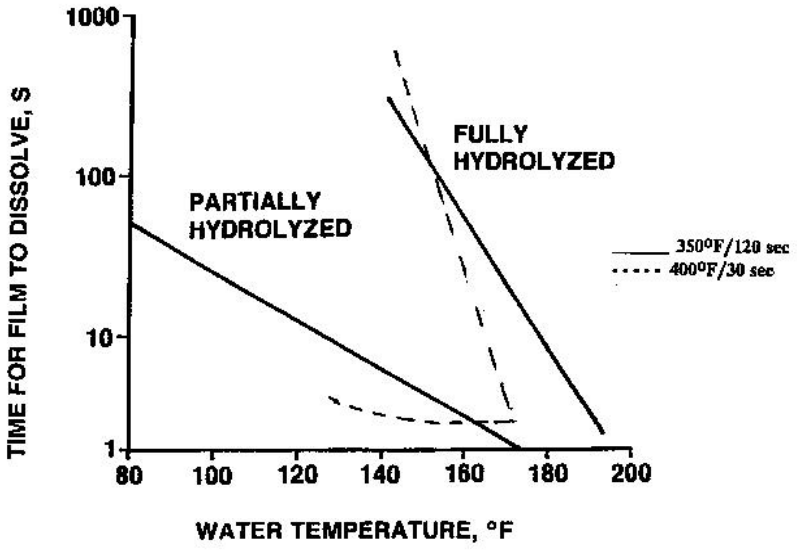


Figure 2.9: Water Solubility of Heat Set PVA Film [25]

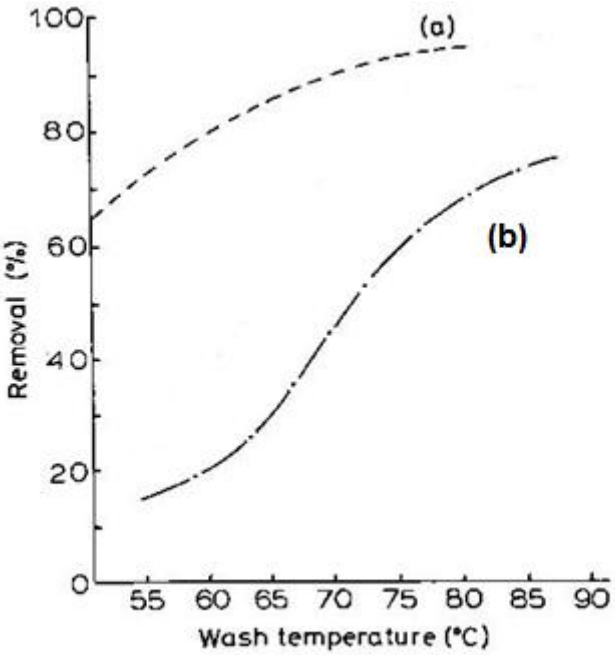


Figure 2.10: Size Removal as a Function of Washing Temperature for (a) Elvanol® T-66 PVA, and (b) Intermediately Hydrolyzed PVA [30]

2.3 Ultrafiltration

2.3.1 Introduction

In UF, a semi-permeable polymeric membrane is used to exclude high molecular weight polymeric size, whereas water, low molecular weight polymer and some cotton impurities pass through it as permeate [10, 12, 22, 31, 36, 37]. UF and related hyperfiltration (HF) processes have been used for textile waste water treatment since 1971 [38], but the first plant for recovery and recycling PVA size was installed in the J. P. Stevens Co. facility at Clemson, S. C. in 1973 [39]. Initially, this technology was used for treating composite textile waste, i.e., water waste from all wet processes [40]. In 1973, Brandon et al. used a dynamic HF membrane specifically for concentration and reuse of dyeing waste water (Figure 2.11) [41, 42]. Brandon observed no detectable difference between samples dyed with water recovered from the UF process and normal plant dye make-up water. The Brandon group results encouraged the eventual use of the UF process in the recovery and recycling of PVA size.

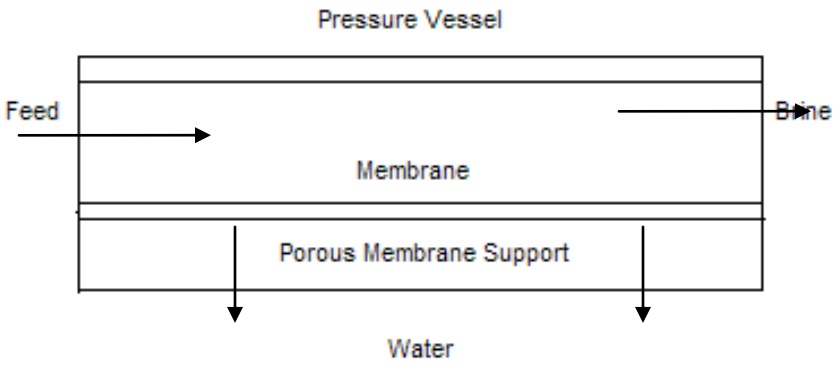


Figure 2.11: Schematic of Hyperfiltration Process [41]

Government regulations targeted to bring the textile discharge of pollutants to zero by 1985 [22] necessitated improvement of the UF size recovery process to make more efficient and economical. In 1979, Porter and Black observed that high molecular weight PVA size is retained by UF membranes [22]. Recovery and reuse of the PVA size reduced the plant COD level up to 93.5%. Potter studied carbon tubular, stainless steel tubular and polyvinyl sulfone spiral-wound film membranes for the recovery of PVA size (Figure 2.12) [5].

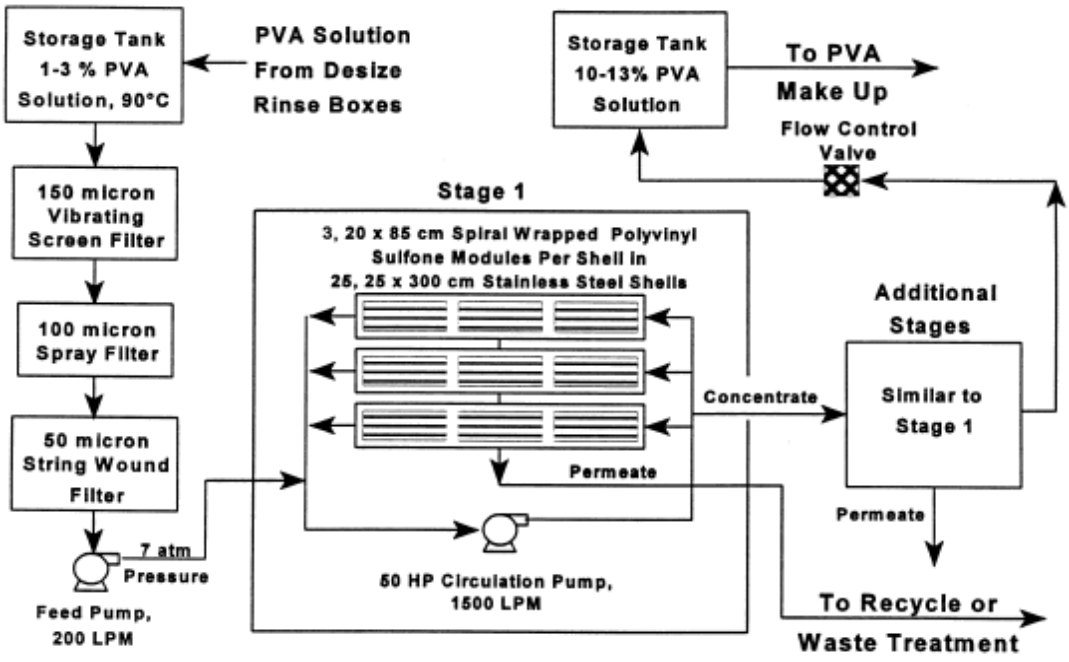


Figure 2.12: Koch Membrane System for Polyvinyl Alcohol Recovery [5]

2.3.2 Recovered Polymer

In UF, a polymeric film membrane is used to separate molecules. This membrane has pores of different sizes and separates molecules according to their physical size. The

desize effluent stream entering the UF process contains water, wax and PVA of molecular dimension 2 Å, 40 Å and 4000-5000 Å, respectively, plus various cotton chemical impurities [30]. PVA has a broad range of molecular weights and in UF water, wax low molecular weight PVA and some cotton chemical impurities pass through the membrane [29]. DuPont determined the effect of UF in PVA-co-methyl methacrylate copolymer recovery. The researchers measured the molecular weights using GPC of the PVA copolymer used in sizing with a number average degree of polymerization of 1000 before slashing, after desizing, and recovered PVA copolymer from UF and UF permeate (Figure 2.13).

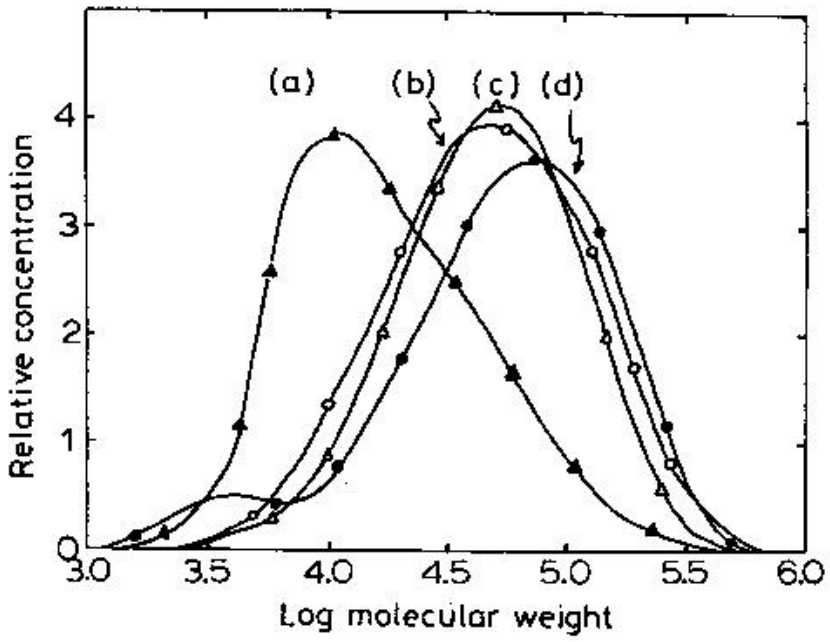


Figure 2.13: Comparison of Molecular Weight Distribution of Elvanol® T-25* Before and After UF Recovery (a) Permeate; (b) Original Copolymer Before Size Preparation; (c) Ultrafiltrate and (d) Feed to the UF Unit [30]

*Elvanol® T-25 is another PVA copolymer in the same series of E. I. DuPont, Co. sizes as its T-66.

The low molecular weight shoulder peak can be seen in the desize effluent stream plot. Shifts in the peak towards low molecular weight shows that the permeate contains low molecular weight polymer. The UF generated concentrate shows a narrowed distribution of the molecular weight, again indicating a loss of low molecular weight PVA to the permeate.

2.3.3 Fouling and Cleaning of UF Membranes

Buckley found fouling of the spiral-wound polysulfone (PS) film UF membrane was a problem that could be controlled by periodic rinsing with hot water and sodium peroxide [12]. The membrane was cleaned at weekly intervals with a 0.5% w/v sodium peroxide solution. However, the efficiency of the PS membrane decreased to 80-90% if cleaned with 0.2M NaOH solution at 25^{o}C and then with hot water at 70–80^{o}C [43]. The authors observed a decrease in membrane efficiency with time upon repeated fouling and cleaning, necessitating periodic replacement. Buckley studied the effect of various cleaning methods on the permeability of the membrane (Figure 2.14) [44].

Buckley and Flemmer developed a mathematical model to calculate the membrane flux [45, 46], and utilized it to evaluate the effect of membrane cleaning and fouling on the efficiency of the UF process. The authors calculated that significant savings could be achieved by optimizing the UF process parameters.

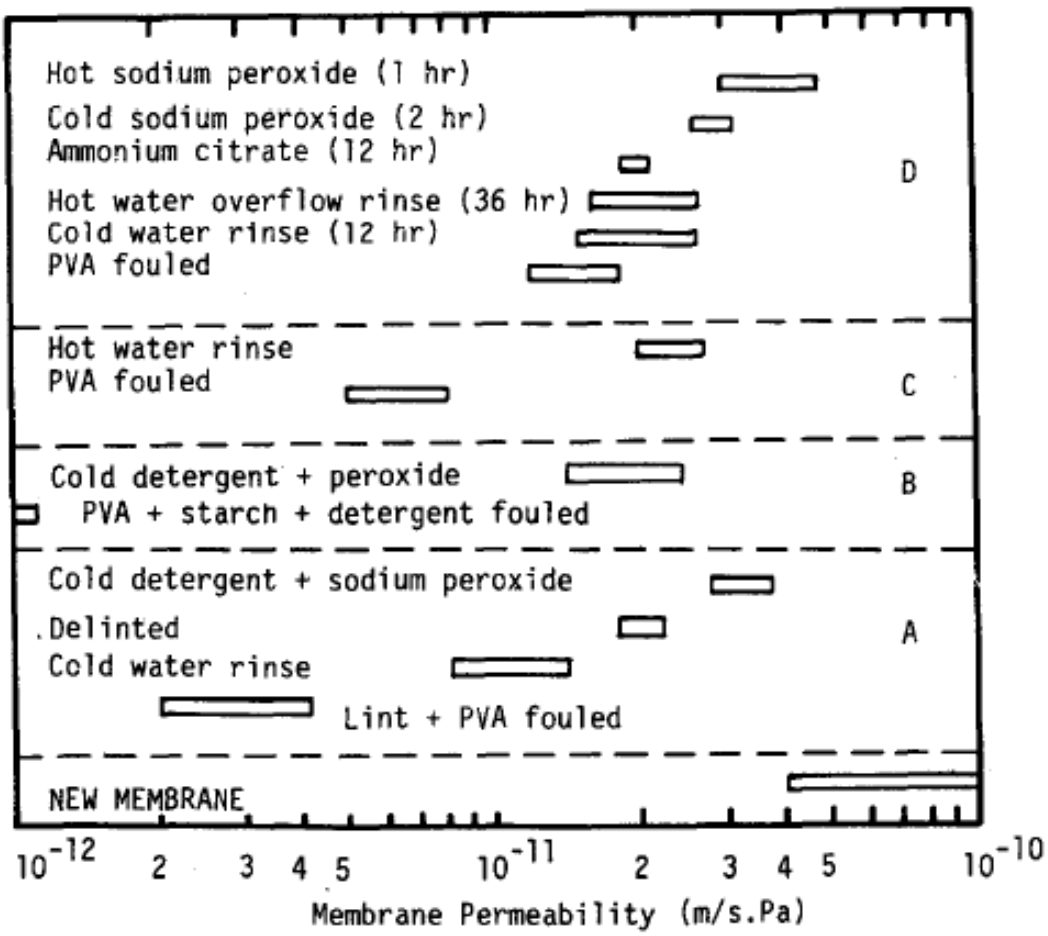


Figure 2.14: Membrane Permeability After Various Cleaning Methods [44]

2.3.4 Effect of Recycled Size on Weaving Efficiency

Buckley et al. [12] and other [32, 47-50] researchers showed the weaving performance of recycled size slashed yarn was actually better than that of the virgin PVA slashed yarn. Langer observed that the recycled size had a narrower molecular weight distribution, as the low molecular weight PVA passed through the membrane and high molecular weight PVA remained in the recycled size [48]. UF recycled PVA slashed yarn showed increases in weaving efficiency of 1-2% over that of virgin PVA. The high molecular weight average, UF-recovered PVA size exhibited improved adhesiveness, and

as a result, recycled PVA slashed yarn also reduced dust emissions in the plant, which not only improved working conditions but also increased the life of the weaving machines [47].

The researchers above did not consider the effect of cotton impurities in the concentrated, recovered size emanating from the UF process. In fact, losing the low molecular weight PVA tail to the permeate should lead to a poorer warp yarn weaving performance and a stiffer size film in the subsequent slashing with recycled size. The increase in weaving performance observed by the various authors was likely due to the occlusion of cotton chemical impurities into the recycled PVA films.

2.3.5 Effect of Variables on UF Process

Lin and Lan studied the effects of membranes and working conditions on the efficiency of the UF process in size recovery [10, 51, 52]. The researchers observed that an increase in temperature, pressure and mixer speed all increased the efficiency of the UF process, but an increase in any of these variables increased the processing cost. They observed that for a UF process, the optimum values of temperature, pressure and mixer speed were 80^{o}C, 200 kPa and 500 rpm, respectively. Temperatures below 80^{o}C decreased the UF efficiency significantly because of an increase in viscosity, whereas, high mixer speeds prevented the blockage of the membrane as it avoided polarization of PVA. The researchers used three types of membranes from the Amicon (Amicon, Inc., Beverly, Massachusetts, USA), two of which were hydrophilic (Amicon YM 30 and YM 100 with 30,000 and 100,000 molecular weight cutoff), and one was hydrophobic (Amicon PM 30 with a 30,000 molecular weight cutoff). The hydrophilic membrane with low molecular weight cut off exhibited good performance, while the hydrophobic

membrane performed well in polymer permeation and retention but had the lowest reusability (Figure 2.15). On the contrary, Andre et al. [49] studied the effect of recycling using UF on properties of recovered size.

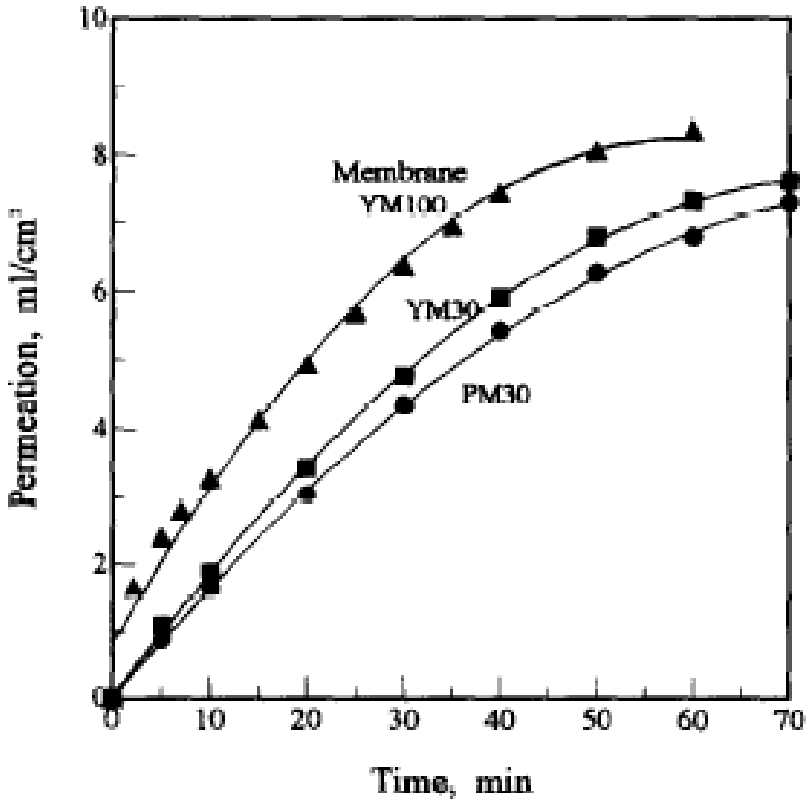


Figure 2.15: Effects of Different Membrane Types on the Permeate Flux at 80°C, 0.135 MPa and 500 rpm Mixer Speed [51]

The authors observed that the viscosity of the size did not change although a large mass of low molecular weight material passed through the membrane. The adhesive power of the size was reduced by 5-7%. Cheng and Pan [53] observed that up to 53% of the UF permeate flux can be enhanced by a gas distributor.

2.3.6 Effect of UF Process Variables on PVA Properties

In the UF process of size recovery and recycling, desize water undergoes thermal stresses and mechanical shear forces, and it contains salts and organic chemical impurities extracted from the cotton under the desizing conditions. Michaela and Wolfgard observed that PVA is not affected by alkali earth salt (calcium chloride dehydrate), whereas it is attacked by alkali salts [54]. The authors also found that the thermal and mechanical stabilities of PVA were good under the UF process conditions. When the recovered PVA size was kept at 80^{o}C for three days in a drying chamber, the viscosity did not change. In another experiment, PVA size was subjected to mechanical shear forces, and it was resistant to degradation under the conditions. The cotton impurities in the regenerated size acted as a good source of nutrients for bacterial growth. Adding 0.5% of 35% hydrogen peroxide to the concentrated size controlled the growth of bacteria.

2.3.7 Efficiency of UF Membrane

The pH of the desize effluent stream affected the efficiency of the UF membrane. Lee et al. observed that the permeation flux was doubled under alkaline conditions [43].

Gunter used KMB polyamide capillary tube membranes for UF size recovery and observed fluid flow through the capillary tube due to hydrostatic pressure, making such membranes economically efficient [6]. Langer studied the effect of concentration of desize effluent on the efficiency of the UF membrane and observed that the efficiency decreased with an increase in concentration (Figure 2.16) [48, 55].

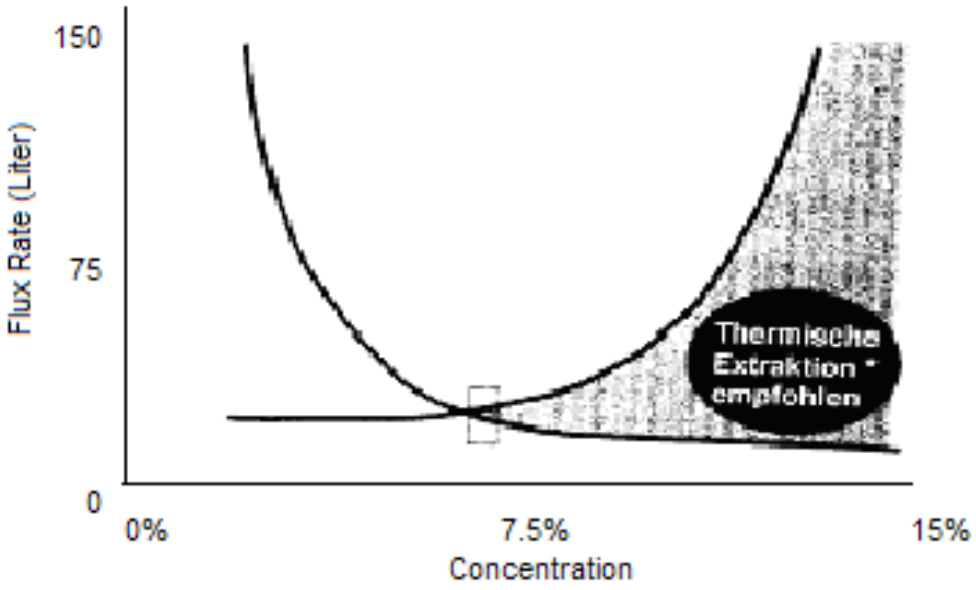


Figure 2.16: Theoretical Flow Rate as a Function of Concentration [48]

Langer attributed this to the formation of a second layer of desize effluent over the UF membrane. The process did not remain economically viable once the desize effluent achieved concentration of 5-7% by weight solids. However, Lee et al. used polysulfone membranes and observed that UF was not economically viable at concentrations above 3% and after achieving the breakeven point, because the low permeation rate cost of energy increased [43]. Langer suggested the use of an evaporative thermal technique for further concentrating the size [48].

Buckley et al. conducted studies for 16 months using a UF pilot plant for closed loop cycling of textile desize effluent [12]. The researchers desized PVA sized cloth at 98^{o}C using 2 l/kg of water. In the UF process, the temperature of desize water was kept at 95^{o}C with concentrations ranging from 1% to 6%. A total of 8% virgin PVA was added to each recycled size formulation. The researchers reported that only 75% of size was recovered using the UF pilot plant. Robinson [56] also reported recovery of PVA

size up to 70% by the UF process, whereas Potter et al. [22], Brandon et al. [38] and Ulrich [57] mentioned PVA recoveries up to 84-90%. The UF process ran for four years without any major failure, which confirmed the reliability of the process.

2.3.8 Economic Benefits of the UF Process

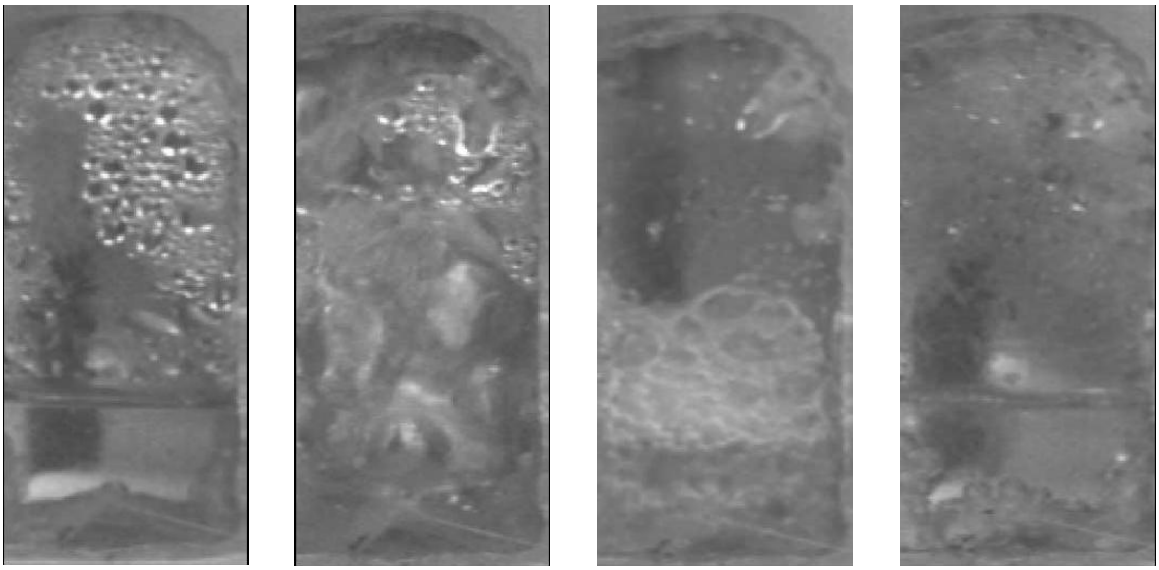
The textile industry uses up to 50% of its energy consumption in heating water [38]. Out of the total effluent load in the finishing process, 50-60% is contributed by the sizing agent [48]. If a UF process of recovery and recycling is used, a plant which uses 346,000 gallons of water per day in conventional desizing can reduce its consumption to 158,000 gallons per day, and energy consumption in heating this water is reduced from 274 million Btu/day to 165 million Btu/day [58]. Potter estimated in 1979 that the U.S. industry consumed 5 trillion Btu of energy in the desizing process [22]. Brandon et al. showed that if an effective UF process is used in PVA size recovery and recycling of water, then savings totaling $79 million in recovered size value and $264 million in energy could be realized annually by the U.S. textile industry [38]. The group also concluded that UF is cost effective if energy recovery is >90%. Potter discussed the economic aspects of the UF process and concluded that the U.S. industry could save up to $500 million a year with incorporation of UF technology for PVA size recovery and reuse [5]. Potter estimated that the payback period of a UF PVA size recovery and recycling process was less than two years. Ulrich, however, estimated it to be less than five years [57].

2.4 Vacuum Flash Evaporation

2.4.1 **Introduction**

In the VFE process, when abrupt pressure drops occur on a water surface, surplus heat in the liquid is transferred into latent heat of vaporization. Following Fick's Law of diffusion, the abrupt drop in pressure increases the mass flow rate 10-15 times more than that of simple thermal evaporation. A super cooled and super heated heterogeneous profile is developed on the liquid surface due to flash evaporation [16]. To make the process more efficient, the liquid is injected into the evaporator by a spray nozzle [17].

Saury et al. conducted a VFE experiment at a water temperature of 40^{o}C, pressure of 50 mbar and superheated temperature of 1K [16]. The initial height of water in the vessel was 15 mm. (Figure 2.17).



(a) t = 0- (b) t = 0+ (c) t = 2s (d) t = 5 min

Figure 2.17: Visualization of VFE Phenomena [16]

The Figure 2.17a photograph was taken just before starting the experiment, where water at 40^{o}C in the flash evaporation vessel was at rest. The Figure 2.17b photograph was taken just after opening the vacuum valve, where the liquid reached a state of turmoil. The Figure 2.17c photograph, which was taken two seconds after the vacuum valve was opened, showed less turmoil, but the water was still boiling. The last photograph (Figure 2.17d) was taken five minutes after opening the vacuum valve, and showed the water again standing at rest. Evaporation was more rapid due to the generated turmoil (Figure 2.17b).

Gopalakrishna [59] determined the mass flow rate experimentally by measuring the height of the liquid in the flash vessel. Saury [11] calculated the mass flow rate for the VFE process using the energy balance (Eqn. 2.1):

$$(m - \delta m)\, c_p\, (T - dT) - m\, c_p\, T - \delta m\, h_{fg} = 0 \quad \text{Eqn. 2.1} \quad [16]$$

c_p Specific heat of liquid [J/kg K]

h_{fg} Latent heat of vaporization [J/kg]

m Mass of liquid [kg]

T Temperature of water [^{o}C]

δm Change in mass [kg]

dT Change in temperature [^{o}C]

and the evaporated mass flow equation (Eqn. 2.2):

$$\dot{m}_{ev} = \frac{dm_{ev}}{dt} = -\rho_1 . A.H \frac{c_p / h_{fg}}{1 + (c_p / h_{fg}).T_o} . \frac{dT}{dt}$$ Eqn. 2.2 [16]

A Horizontal cross-sectional area of flash chamber [m^2]

c_p Specific heat of liquid [J/kg K]

H Height of liquid [m]

h_{fg} Latent heat of vaporization [J/kg]

m_{ev} Evaporated mass of liquid [kg]

$\dot{m}_{ev}$ Instantaneous evaporated mass flow [kg/s]

T_o Initial temperature of water [^oC]

ρ1 Density of liquid [kg/m3]

2.4.2 Effect of VFE Process Variables on Mass Flow

Saury plotted Figures 2.18 and 2.19 using an evaporated mass flow rate equation, and observed that the evaporated mass of water initially increased with time, but remained constant after 6 seconds of vacuum flash evaporation [16]. Figures 2.18 and 2.19 show that the evaporated mass and evaporated mass flow rate decreased with time:

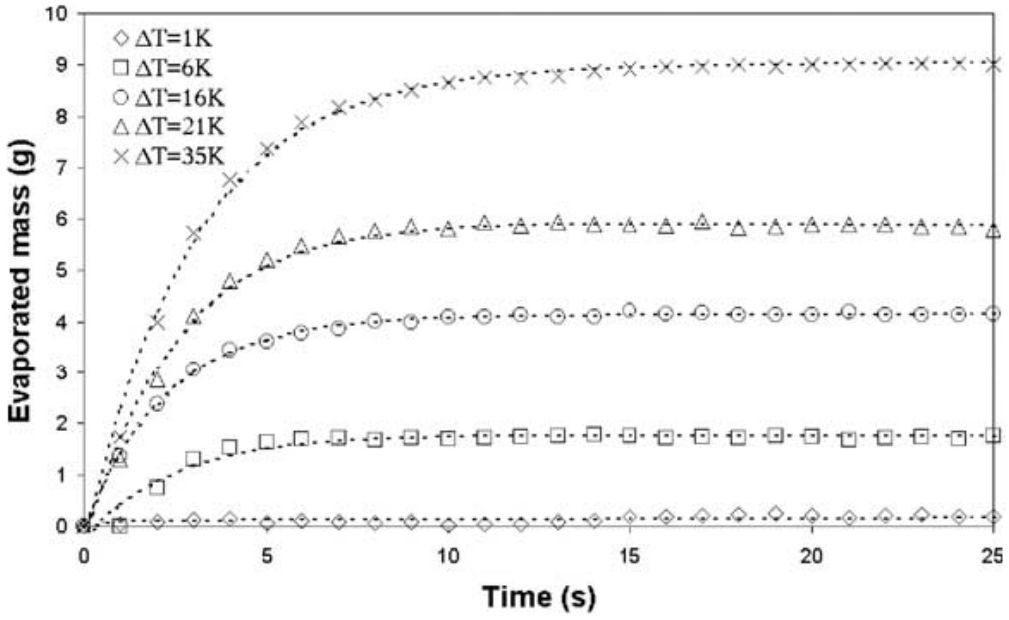


Figure 2.18: Evolution of m_{ev} vs. Time at a Pressure of 50 mbar [16]

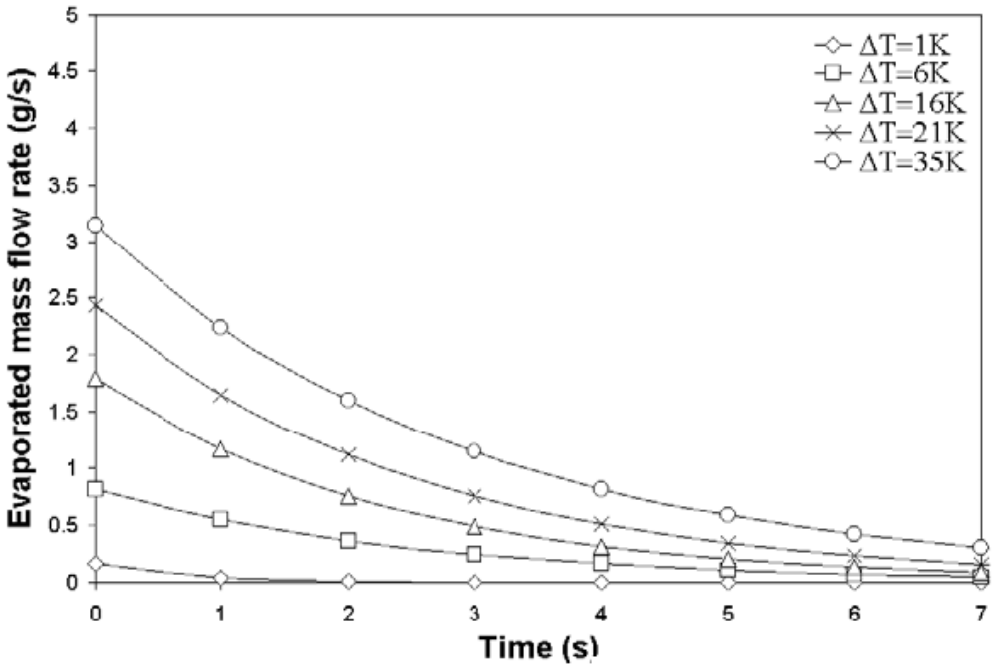


Figure 2.19: Evaporated Mass Flow Rate vs. Time at 50 mbar Pressures [16]

Saury also observed that the evaporated mass increased with an increase in initial temperature, but decreased with an increase in initial pressure (Figure 2.20).

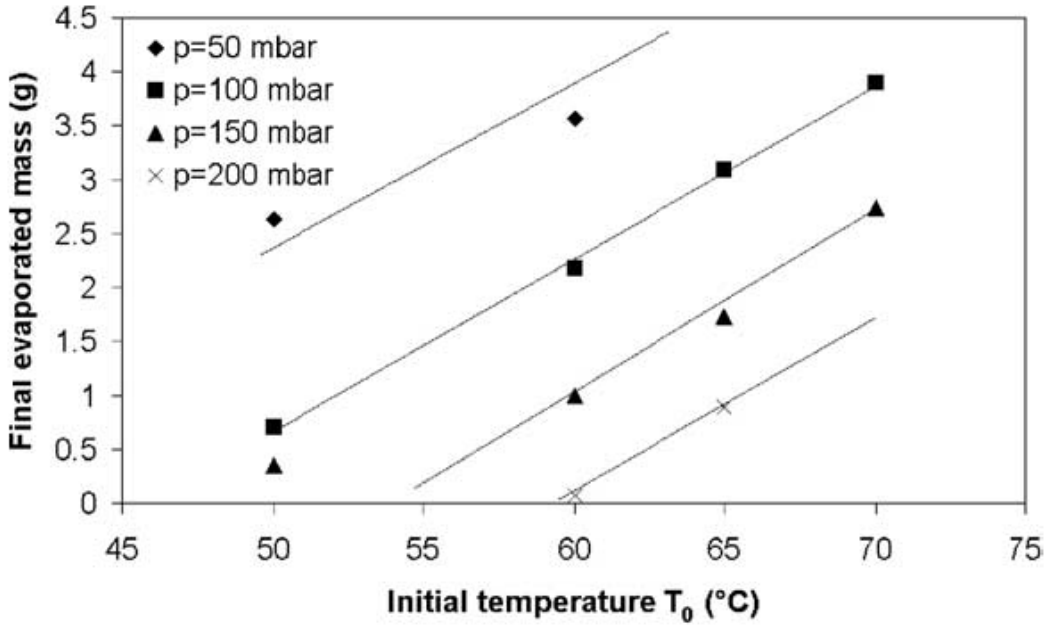


Figure 2.20: Evolution of Evaporated Mass vs. Initial Temperature [16]

2.4.3 Economic Benefits of the VFE Process

Heat energy recovered in the VFE process is up to 95%, and the turbulence in the recycled stream reduces fouling inside the heat exchanger [19]. The processes operate at temperatures as low as 35^{o}C [18, 20, 60, 61]. Some of the applications of the VFE concentration process are desalination, distillation of 1,4-butanediol, concentration of clay slurries, removal of volatile matter from polymer solutions and treatment of waste streams from polyvinyl acetate glue, oil refinery, rolling stock, etc., processes [13-15, 18-20, 60-62]. According to VACOM, LLC and the Led Italia Co., the energy cost of operating a plant-scale VFE system is $0.0125/feed gallon (concentrating liquid from 1%

to 25% [1]) and $13.55/feed ton, respectively, with raw ROI of less than a year with both company systems. A VFE process can increase concentration of the target polymer up to 90 - 95% [60, 63]. One gallon of desize water contains 37.8 grams of PVA if the initial concentration of PVA is 1%, with a value of $0.08316 (considering a virgin PVA cost $1/lb). If the desize effluent of a large operating plant is 100,000 gallons/day and the plant operates 350 days/year, projected savings in recycled PVA alone would be $2.9M/year, coupled with hot water savings of approximately ~100,000 gallons/day.

2.4.4 VFE Plant Operations

A VFE unit consists mainly of three components: feeding unit, evaporation unit and heat exchanger (Figure 2.21). The maximum and minimum levels of liquid in the evaporator are fixed, and when the level goes below the minimum level, the feeding unit receives the signal and automatically fills the evaporator. The feeding unit feeds directly into the evaporator or via a heat exchanger, depending on the temperature of the feed liquid and the temperature inside the evaporator. The liquid in the evaporation unit is exposed to a sudden pressure drop and evaporates; this pressure is controlled by a flash valve. Evaporated steam passes from the evaporation unit to the heat exchanger. When the desired concentration of PVA is achieved, the concentrate is drained from the evaporator and passed to the slashing operation. The temperature of the liquid inside the evaporator is maintained by passing the liquid continuously through the heat exchanger. The steam is passed through the heat exchanger and condensed, resulting in a stream of clean, hot water that has unrestricted reuse in the plant's wet processes.

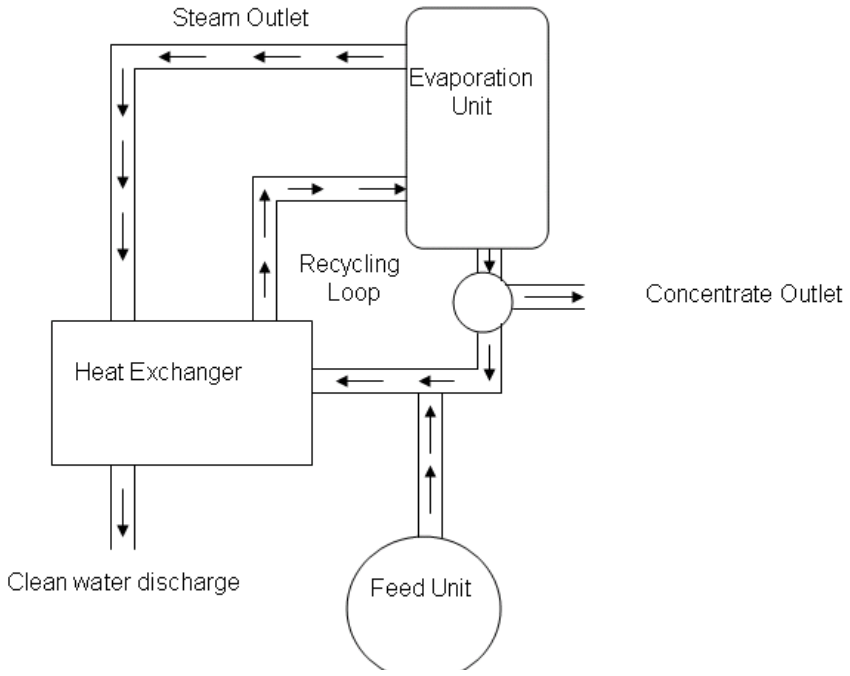


Figure 2.21: Flow Chart of Vacuum Flash Evaporation Process

CHAPTER 3

OBJECTIVES AND TECHNICAL APPROACH

3.1 Objectives

In earlier research on the UF process of recovery and recycling of PVA size, more emphasis was given to the process itself, but little attention was given to the properties of the recovered size. The main objectives of this research were:

- To study the technical and economic feasibilities of the VFE process in the concentration/recovery and subsequent recycling of PVA size, and how the VFE process can avoid the major disadvantages of the analogous UF process.
- To investigate the recycled PVA polymer plus cotton chemical impurity blended size, and determine the effects of film property changes as a function of recycle sequence number, i.e., increasing impurity level.
- To study the effects of cotton impurities in recycled PVA size on the weaving performance of slashed warp yarns.
- To study the effects of cotton impurities along with wax in the size formulation on the film properties.
- To study the effects of cotton impurities along with wax in recycled PVA size on the weaving performance of slashed yarns.

- To demonstrate the feasibility of the VFE process to concentrate and recover PVA size, using a Webtex Pilot (12 end warp) Slasher to slash cotton towel pile and ground yarns.

3.2 Technical Approach

The research was divided into four phases:

1. To determine the effects of cotton impurities on recycled size films and slashed yarns.
2. To determine the effects of cotton impurities, wax and their combinations on recycled size films and slashed yarns.
3. To conduct scale up, proof of concept trials by applying the optimized bench scale results to a Webtex Pilot (12 end warp) Slasher.
4. To calculate the economic feasibility of incorporating the demonstrated VFE PVA size recovery/reuse process into a model plant.

3.2.1 Effect of Cotton Impurities on Recycled Size Films and Slashed Yarns

The first phase of the research investigated the effects of cotton impurities on recycled PVA polymer and determined the film and slashed yarn properties as a function of recycle sequence number. The tests conducted to determine cast, recycled size film and slashed yarn properties are summarized in Table 3.1. Film and slashed yarn samples were made from simulated, recycled PVA solutions. In the VFE process, water is evaporated and the concentrated solution consists of PVA, wax and extracted cotton chemical impurities. Cotton chemical impurities are extracted from the slashed yarns

during the desizing process. In the simulated samples, yarn impurities were first extracted from cotton yarns by conducting the desizing process on greige yarns, and the concentrated impurity solution was mixed with virgin PVA powder to reach established concentrations of both. Impurity levels of 0%, 14.3%, 25%, 33.3% and 40% by weight solids were utilized for the recycled PVA film and slashed yarn preparations. Recycled PVA films were assessed for tensile properties (breaking strength, elongation at break, elastic modulus, etc.). As slashed warp yarns undergo repeated cycles of stress and strain during the weaving process, their tensile properties were also assessed. Other important properties such as film wettability, bust rod resistance and viscosity were tested. The slashed yarns were desized under optimized conditions, and the ease of the desizing process was measured by film wettability.

Industry normally controls the slashing process through size formulation viscosity/concentration, so the effects that recycling the PVA/cotton impurity had on size solution viscosity were established. In slashing, the sheet of yarns exiting from squeeze rollers is dried on steam cans. In this sheet, some of the yarns are stuck together by bridged PVA film. To individualize the sized yarn, this sheet is divided into two sheets, or leases, of alternate yarn by a metal rod called a bust or leasing rod. The bust rod is located between the yarn sheets or leases. Most of the yarn breaks and hairiness generation take place at this point of the slashing process, so the bust rod resistance was studied.

Table 3.1: Experimental Plan Phase 1: Effects of Cotton Chemical Impurities Concentration on Films and Slashed Yarn Properties

Test	Materials	Sample Compositions	Observation	Purpose
Tensile Properties	Virgin and Recycled PVA Size Film	Five Impurities Concentration: 0%, 14.3%, 25%, 33.3% and 40%	Change in Breaking Strength, Elongation at Break and Elastic Modulus with impurities	Important for Weave Ability
Contact Angle	Virgin and Recycled PVA Size Film	Five Impurities Concentration: 0%, 14.3%, 25%, 33.3% and 40%	Change in Contact Angle with Impurities	Good Desizing Properties are Required
Viscometry	Virgin and Recycled PVA Size Film	Five Impurities Concentration: 0%, 14.3%, 25%, 33.3% and 40%	Change in Viscosity with Impurities	Industry Control Sizing Process from its Viscosity
Tensile Properties	Slashed Yarn with Recycled Size	Five Impurities Concentration: 0%, 14.3%, 25%, 33.3% and 40%	Change in Tenacity and Work of Rupture with Impurity	Important for Weave Ability

Table 3.1 (contd.): Experimental Plan 1: Effects of Cotton Chemical Impurities Concentration on Films and Slashed Yarn Properties

Test	Materials	Sample Compositions	Observation	Purpose
Size Add-On	Slashed Yarn with Recycled Size	Five Impurities Concentration: 0%, 14.3%, 25%, 33.3% and 40%	Change in Size Add-On with Impurities	Size Yarn Properties Depend on Size Add-On
Bust Rod Resistance	Slashed Yarn with Recycled Size	Five Impurities Concentration: 0%, 14.3%, 25%, 33.3% and 40%	Change in Bust Rod Resistance with Impurities	Most of the Breakages Take Place at Bust Rod

3.2.2 Effect of Cotton Impurities, Wax and their Combinations on Recycled Size Films and Slashed Yarns

The second phase of this research studied the effect of cotton chemical impurities on recycled PVA and slashed yarn along with the wax percentage, because wax is used in moderate percentages (8% of PVA recommended) in the conventional, T-66 PVA-only slashing formulation. Experiments were designed at four levels of wax and four levels of impurities as shown in Table 3.2. Slashing solutions were simulated by mixing known quantities of wax, T-66 PVA and cotton impurities. Sixteen samples of yarns were slashed utilizing the two yarn end, bench-scale slasher (Section 4.3.1.1). Films were cast from final, recycled size formulations at all possible combinations of wax and cotton chemical impurity percentages (Table 3.2).

Table 3.2: Combination of Wax and Impurity Percentages for Film Preparation

Impurities-Wax*	0% wax	4% wax	8% wax	12% wax
0% Impurities	0-0	0-4	0-8	0-12
10% Impurities	10-0	10-4	10-8	10-12
25% Impurities	25-0	25-4	25-8	25-12
40% Impurities	40-0	40-4	40-8	40-12

*The percentage of wax is based on the mass of PVA in the blend size formulation.

Films were tested for their tensile properties, whereas slashed yarns were tested for tensile properties, bust rod resistance, size add-on, hairiness, abrasion cycles to first yarn breaks, etc. (Table 3.3).

Table 3.3: Experimental Plan: Effects of Cotton Chemical Impurities Concentration on Films and Slashed Yarns Properties

Test	Materials	Sample Compositions	Observation	Purpose
Tensile Properties	Virgin and Recycled PVA Size Film	Four Impurities Concentration: 0%, 10%, 25%, 40% Wax Percentages: 0%, 4%, 8% and 12%	Change in Breaking Strength, Elongation at Break and Elastic Modulus with impurities	Important for Weave Ability
Viscometry	Virgin and Recycled PVA Size Film	Four Impurities Concentration: 0%, 10%, 25%, 40% Wax Percentages: 0%, 4%, 8% and 12%	Change in Viscosity with Impurities	Industry Control Sizing Process from its Viscosity
Tensile Properties	Slashed Yarn with Different Recycled Size	Four Impurities Concentration: 0%, 10%, 25%, 40% Wax Percentages: 0%, 4%, 8% and 12%	Change in Tenacity and Work of Rupture with Impurities	Important for Weave Ability

Table 3.3 (contd.): Experimental Plan: Effects of Cotton Chemical Impurities Concentration on Films and Slashed Yarns Properties

Test	Materials	Sample Compositions	Observation	Purpose
Size Add-On	Slashed Yarn with Different Recycled Size	Four Impurities Concentration: 0%, 10%, 25%, 40% Wax Percentages: 0%, 4%, 8% and 12%	Change in Size Add-On with Impurities	Size Yarn Properties Depend on Size Add-On
Bust Rod Resistance	Slashed Yarn with Different Recycled Size	Four Impurities Concentration: 0%, 10%, 25%, 40% Wax Percentages: 0%, 4%, 8% and 12%	Change in Bust Rod Resistance with Impurities	Most of the Breakages Takes Place at Bust Rod

Table 3.3 (contd.): Experimental Plan: Effects of Cotton Chemical Impurities Concentration on Films and Slashed Yarns Properties

Test	Materials	Sample Compositions	Observation	Purpose
Hairiness	Slashed Yarn with Different Recycled Size	Four Impurities Concentration: 0%, 10%, 25%, 40% Wax Percentages: 0%, 4%, 8% and 12%	Change in Hairiness with Impurities	Hairiness Cause Breakage on Loom
Abrasion Cycles to First Yarn Breaks	Slashed Yarn with Different Recycled Size	Four Impurities Concentration: 0%, 10%, 25%, 40% Wax Percentages: 0%, 4%, 8% and 12%	Change in Abrasion Cycles with Impurities	Main Concern of Sizing to Improve Weave Ability

3.2.3 Proof of Concept Trials Conducted on Pilot Slasher

In the third phase of this research, optimized results obtained from the bench top research were applied in scale up studies using the continuous Webtex© Pilot Slasher (Section 4.3.3). The cotton chemical impurity concentration plateau in the recycled size was achieved in ~five slashing cycles. In consultation with WestPoint Homes, size solids add-ons of 10% and 3% by yarn weight were fixed for ground and pile yarns respectively. Conventional residential towels manufactured by WestPoint Homes (WPH) have ground, pile and filling yarns in a 1:6:1 mass ratio, respectively. Ground and pile yarns were slashed in adequate volumes to generate the respective masses of slashed yarns corresponding to the WPH towel ratio. The first slashing cycle was conducted as a conventional slashing (93% T-66 PVA/7% Seyco Superwax S), then five slashing cycles were conducted using recovered plus virgin PVA formulations (no wax was added to the recycle formulations that contained the extracted cotton impurities). A 10 ml aliquot of a 4 g/l solution of C.I. Basic Violet 10 dye was added to each size formulation to provide a visual interpretation of size penetration into the yarn diameters.

In towels, ground and pile yarns are slashed, whereas filling yarn is greige (unsized), so when desizing towels, filling yarn impurities are also extracted into the desize effluent stream. Towel desizing was simulated by mixing slashed ground, slashed pile and greige filling yarns in the same mass ratio (1:6:1) as existing in WPH's residential towels. After VFE concentration of the desize streams and addition of the optimized mass of virgin T-66 PVA to complete the size formulations for the next slashing cycles, films were cast from the final size formulation, and their breaking strengths, elastic moduli and elongations to break were all tested. Slashed pile and ground

yarn physical properties, i.e., tenacity, load at break, elongation at break, work of rupture, bending length, abrasion resistance, degree of hairiness, size penetration, yarn color and size add-on, were all quantified (Table 3.4).

Table 3.4: Experimental Plan: Effects of Cotton Chemical Impurities Concentration on Films and Slashed Yarns Properties

Test	Materials	Sample Compositions	Observation	Purpose
Tensile Properties	Virgin and Recycled PVA Size Film	First Conventional Slashing Followed by Five Recycle Slashing for both Pile and Ground Yarn	Change in Breaking Strength, Elongation at Break and Elastic Modulus with Recycling	Important for Weave Ability
Tensile Properties	Slashed Yarn with Recycled Size	First Conventional Slashing Followed by Five Recycle Slashing for both Pile and Ground Yarn	Change in Load at Break, Elongation at Break, Tenacity and Work of Rupture with Recycling	Important for Weave Ability
Size Add-On	Slashed Yarn with Recycled Size	First Conventional Slashing Followed by Five Recycle Slashing for both Pile and Ground Yarn	Change in Size Add-On with Recyling/Impurities	Size Yarn Properties Depend on Size Add-On

Table 3.4 (contd.): Experimental Plan: Effects of Cotton Chemical Impurities Concentration on Films and Slashed Yarns Properties

Test	Materials	Sample Compositions	Observation	Purpose
Bust Rod Resistance	Slashed Yarn with Recycled Size	First Conventional Slashing Followed by Five Recycle Slashing for both Pile and Ground Yarn	Change in Bust Rod Resistance with Recycling	Most of the Breakages Takes Place at Bust Rod
Microscopy	Slashed Yarn with Different Recycled Size	First Conventional Slashing Followed by Five Recycle Slashing for both Pile and Ground Yarn	Change in Size Penetration with Recycling/Impurities	Size Penetration Important from Desizing Point of View
Hairiness	Slashed Yarn with Recycled Size	First Conventional Slashing Followed by Five Recycle Slashing for both Pile and Ground Yarn	Change in Hairiness with Recycling/Impurities	Hairiness Cause Breakage on Loom
Abrasion Cycles to First Yarn Breaks	Slashed Yarn with Recycled Size	First Conventional Slashing Followed by Five Recycle Slashing for both Pile and Ground Yarn	Change in Abrasion Cycles with Recycling/Impurities	Main Concern of Sizing to Improve Weave Ability

Table 3.4. (contd.): Experimental Plan: Effects of Cotton Chemical Impurities Concentration on Films and Slashed Yarns Properties

Test	**Materials**	**Sample Compositions**	**Observation**	**Purpose**
TGA	Desize Solid	Five Disizing Cycles	Change in Impurity with Desizing	Impurity Percentage in Slashing Solution
Dilute Solution Viscometry	PVA and Desize Solid	Desize solid	Change in Intrinsic Viscosity with Recyling/Impurity	Change in Molecular Weight
Desizing Efficiency	Desize Yarn/Solid	Five Desizing Cycles	Percentage Solid Remove in Desizing	Further Processing of Fabric
Color Variation	Desize Yarn	Five Desizing Cycles	Desize Yarn Color	Further Processing of Fabric
Bending Length	Slashed Yarn with Recycled Size	First Conventional Slashing Followed by Five Recycle Slashing for both Pile and Ground Yarn	Change in Bending Length with Recycling/Impurities	Slashing Pile Yarn

3.2.4 Economic Feasibility

Determination of the developed VFE PVA recovery and recycling process' economic feasibility was conducted in consultation with VFE instrument manufacturer VACOM, LLC. A model industrial plant producing desize effluent at a rate of ~100,000 gallons per day was considered and savings from incorporation of the VFE technology for PVA size recovery and recycling over the conventional PVA/starch/wax process with no size recycling was calculated.

CHAPTER 4

RAW MATERIALS AND EXPERIMENTAL PROCEDURES

4.1 Raw Materials

Slashing Material (Size)

PVA-based copolymer

Grade: Elvanol T-66®

Lot No: L5K041 (2006), L7K010 (2008)

Manufacturer: E. I. DuPont Co.,

Weight average molecular weight: 33,500

Number average molecular weight: 65,000

Degree of polymerization: 737

Sol. Viscosity (cP): 13.5 (4% solid, 23^{o}C)

Wax

Grade : Seyco Superwax S

Manufacturer: Seydel-Woolley & Co, Inc.

Yarn

Type: Rotor Spun

Use: Ground

Cotton count: 9.5's

Supplier: Spring Industries

Type: Rotor Spun

Use: Pile

Cotton count: 12’s

Supplier: Spring Industries

Type: Rotor Spun

Use: Ground, Filling

Cotton count: 10’s

Supplier: Frontier Spinning Mills

Type: Rotor Spun

Use: Pile

Cotton count: 12’s

Supplier: Frontier Spinning Mills

Tracer Dye

Trade Name: C.I. Basic Violet 10

CAS #: [81-88-9]

Supplier: Organic Dyestuffs Corporation, Rhode Island, USA

Antibacterial Agent

Trade Name: Bioban DXN

Manufacturer: Dow Chemical Company, Midland

4.2 Equipment

Polymer Film Formation

Model: Auto-Draw III

Manufacturer: Industry Tech, Florida

Bench Yarn Slasher (2 End Slasher)

Manufacturer: Developed in-house using old machine parts

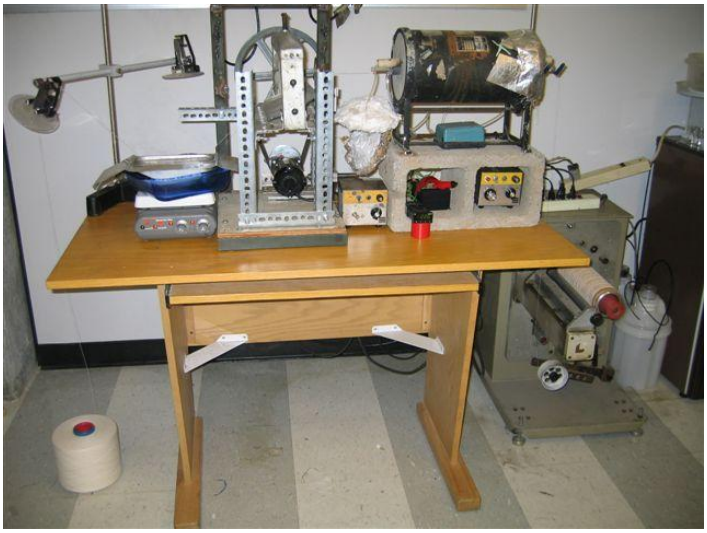


Figure 4.1: Photograph of the Two-End Bench Slasher

Yarn Slashing Machine (at UGA, Athens, GA)

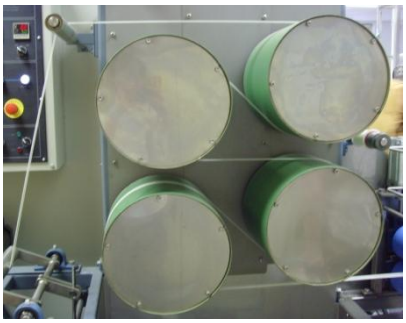
Model: Webtex

Manufacturer: Alma Works Todmorden, Lancs

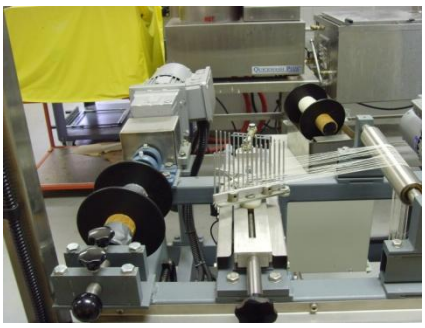
(a) Side View of Webtex Slasher

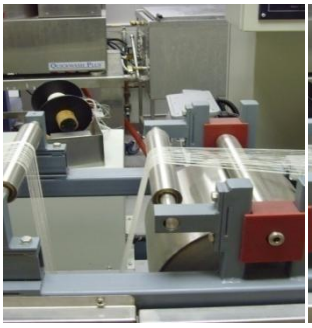
(b) Size Box

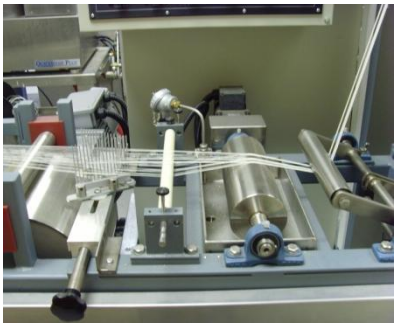
(c) Warp Creel



(d) Drying Cans (e) Squeeze Roller







(f) Winding Spool (g) Tension Rod (h) Bust Rod

Figure 4.2: Sections of Webtex© Slasher

Thermogravimetric Analyzer (TGA)

Model: TGAQ5000-0307

Manufacturer: TA Instrument

Instron

Model: 5567

Manufacturer: Instron, Norwood

Toray Fray Counter

Model: DT-104 with S-Head

Manufacturer: Toray Industries, Inc. Charlotte

Sulzer Ruti Webtester,

Model: Reutlinzer Webtester

Manufacturer: Sulzer Ruti Machinery Works Ltd

Bending Stiffness

Model: FRL Cantilever Bending Tester

Manufacturer: Testing Machines Inc. New York

Contact Angle

Model: VCA Optima

Manufacturer: AST Products Inc.

Hunter MiniScan Portable Spectrocolorimeter

Model: MiniScan MS/S-4000L

Manufacturer: Hunter Associates Laboratory Inc. Virginia

Rotary Evaporator

Model: Heidolph Collegiate Laborota 4000 G1

Manufacturer: Brinkmann

Vacuum Oven

Model: M-3608-5

Manufacturer: Lab Line Instruments Inc. Melrose

Oven

Model: Isotemp Oven

Manufacturer: Fisher Scientific

Viscometer

Model: DV-1

Manufacturer: Brookfield

Microscope

Model: LEICA DM IRM, Software Image Pro 6.2

Manufacturer: Leica Microsystems

4.3 Experimental Procedures

4.3.1 Size Formulation

The size formulation and make-up procedure were supplied by the T-66 PVA size manufacturer, E. I. DuPont Co. [64]. The required amount of water was stirred with a

magnetic bar in a beaker at room temperature and measured quantities of the powdered Elvanol T-66 PVA and flaked Seyco Superwax S were sequentially added. The temperature of the beaker was raised to 90^{o}C via hot plate, and maintained at this temperature with stirring for 30 min.

4.3.1.1 Simulated Recycled Slashing Solution

In VFE, excess water is evaporated to steam, and the size concentrate stream containing extracted cotton impurities exits the process. Cotton impurities alone were obtained by desizing greige yarn using the initially-developed, two-step desizing method (4.3.4.1). Known quantities of cotton impurities and T-66 PVA were mixed with water to generate a simulated, recycled size formulation. Industry controls the slashing process either by controlling viscosity or controlling concentration of the slashing solution. Viscosity of the size formulation was kept constant at 10 cP. Other conditions and procedures for making size formulations were the same as detailed by the E. I. DuPont Co. [64].

4.3.1.2 Recycled Size Formulation

In discussions with WPH, residential towel compositions were manufactured in the mass ratio of 1:6:1, respectively, for ground, pile and filling yarns [28]. In the towel, only ground and pile yarns are slashed, whereas filling yarn remains greige. In this work, the yarns were mixed in the same mass ratio as the WPH residential towel and desized using the developed, three-step desizing process (Section 4.3.4.2). Solids in the desize effluent were calculated (Section 4.3.7), and the effluent stream was then divided in the volume ratio 5:9 for ground yarn and pile yarn, respectively. The desize effluent stream fractions were then concentrated using the Rotary Evaporator to 2.4% and 6% total solids

concentrations for pile and ground yarn, respectively (Section 4.3.5), bringing the solutions to the calculated final volumes required for the recycled size formulations. Calculated quantities of virgin PVA were added in the concentrated effluent fractions for pile and ground yarn to generate the final size formulations for the subsequent slashing cycles. The temperature of the size formulations was raised to 90^{o}C and maintained for 30 minutes, and the tracer dye was then added to the formulation. The solids concentrations were kept constant at 10% and 3% w/v for ground and pile yarns, respectively. Ground and pile yarns were slashed using their respective solutions, and the desize stream solids concentration/recycled size reuse process was then repeated five times with each yarn type.

4.3.2 Cotton Chemical Impurities

The total mass of cotton chemical impurities that were released during desizing was calculated using a mass balance. Greige cotton yarn was dried in an oven at 50^{o}C for two hours and then conditioned at 72^{o}F and 65% RH for 24 hours. The yarn was weighed and then desized. The desized yarn was dried in the oven and conditioned as above. The dried and conditioned desized yarn was weighed again, and the percentage loss in weight was calculated. The percentage by yarn weight of cotton impurities extracted from the yarns corresponded to the percentage loss in yarn weight occurring in the desize process.

The cotton impurities percentage by weight extracted from the greige yarn under the desizing conditions was confirmed through a different route by evaporating the water from the desize effluent stream in a convection oven. A clean, empty beaker with aluminum foil was dried in the oven. The beaker was sealed with the aluminum foil and weighed after cooling for 10 minutes. The aluminum foil was removed from the beaker,

and the desize effluent stream water was evaporated from the beaker first in the convection oven and then in a vacuum oven. After achieving total dryness of the residual cotton impurities, the beaker was sealed with the aluminum foil, cooled for 10 minutes, and weighed again. The percentage of cotton impurities was calculated from the dry impurities' mass weight.

4.3.3 Yarn Slashing

Slashing experiments were conducted using two slashing lines. Bench top experiments were conducted using the two-yarn-end bench slasher (Figures 4.1 and 4.3). Simulated recycled size formulations were prepared by mixing known quantities of T-66 PVA and cotton impurities. Size formulation viscosity was kept constant at 10 cP. Size box temperature was maintained at 70^{o}C. Slashing speed was kept constant, and the slashed yarn was passed through squeeze rolls at constant pressure to attain the proscribed wet pickup. Finally, the slashed yarns passed through a 12 inch tube furnace set at ~200^{o}C for drying. Over-drying of the slashed yarn was prevented by appropriately synchronizing the oven temperature.

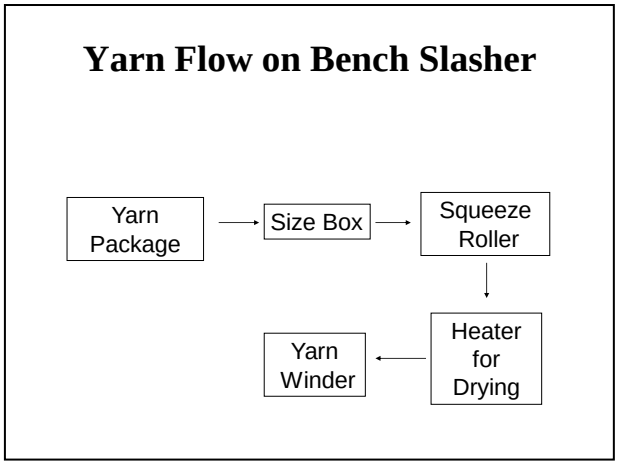


Figure 4.3: Yarn Flow Chart of the Bench Slasher

In the scale-up experiments, the Webtex© Pilot Slasher was utilized to slash 12 warp yarn ends (Figure 4.2). The maximum number of yarns ends that were allowed on the slasher (30) were reduced to 12 and new small size box was fabricated because of the following problems:

- The full Webtex size box temperature was not uniform.
- No stirring mechanism was built into the size box.
- Due to the large volume of the size box, evaporation was rapid at the application temperature (70^{o}C), rendering control of the size formulation concentrations difficult.
- Because of the large size box, a huge quantity of yarn was required to be slashed and then desized, generating a large volume of desize effluent. Evaporating a high volume of desized effluent was difficult and time-consuming on the simulated VFE, rotary evaporator system.

The level of the size formulation in the box was maintained and its temperature was kept constant at 70^{o}C with continuous stirring using a hot plate magnetic stirrer with Teflon©-coated bar. Impregnated yarn was squeezed by rolls to the proscribed wet pickup (~100%) at constant, minimum pressure. The slashed yarns were then dried in line on the electric-fired drying cans. Four drying cans were traversed in series, and the can temperatures were controlled in the 120-140^{o}C range. The slashed yarn was passed successfully from the drying cans through the slasher's guides, bust rods, tensioning bar and finally to the winding spool of the line. Size formulation concentrations for the ground and pile yarns were kept constant at 10% and 3% w/v, respectively. The linear

yarn speed (10 m/minute) was kept constant for slashing ground and pile yarns to achieve the required add-ons. Size solids add-ons required for pile and ground yarns were also 3% and 10% on the weight of the yarns, respectively. Size solids add-ons were checked intermittently by physically removing slashed yarn samples just after the squeeze rollers and measuring their weights and lengths to calculate the add-ons:

$$\text{Size addon} = \frac{W - D}{D} * \frac{S}{100} * 100 \quad \text{Eqn. (4.1)}$$

W: Wet Yarn Weight / Length

D: Dry Yarn Weight / Length

S: Size Formulation Concentration

4.3.4 Yarn Desizing

Desizing process conditions were optimized so that ≥95% of the size was removed from the slashed yarns. Two desizing methods were developed. Both methods removed up to ≥95% of the size and the same ~2.3% percentage of cotton chemical impurities based on yarn weight. The first developed desizing method was a two-step process, utilizing fresh water in both steps. After visiting WPH, a new desizing method was developed which better simulated the WPH desizing process. The second method was a three-step process, utilizing fresh and used (recycled) wash water.

4.3.4.1 Two-Step Yarn Desizing Process

Slashed yarn was desized in two steps as shown in Figure 4.4. In the first step, the liquor ratio was maintained at 20:1. The desized bath was heated to 95^{o}C and sized

yarn was then immersed into it. Yarn in the water was stirred continuously for four minutes. Yarn was then taken out and squeezed by hand to remove the excess liquid. In the second step, the liquor ratio was maintained at 10:1. The desize bath was heated to 85^{o}C, and then the first-step desized yarn was immersed into it. The bath was stirred continuously for two minutes. The yarn was then removed and squeezed by hand. The desize effluent streams from both steps were collected and combined for concentration/recycling.

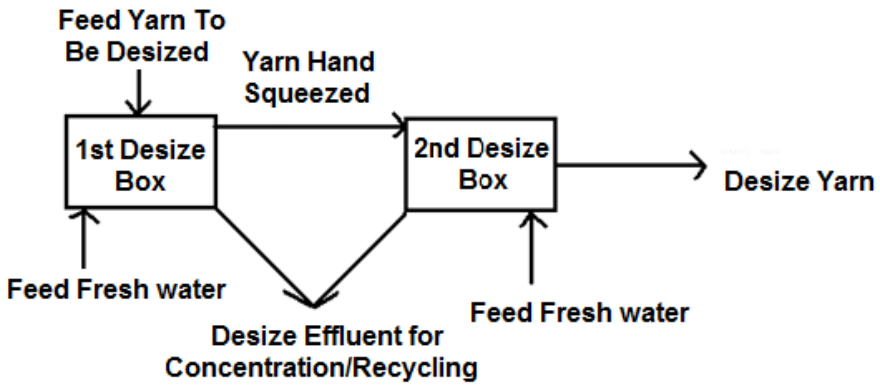


Figure 4.4: Line Diagram of Two-Step Desizing Process

4.3.4.2 Three-Step Desizing Process

Desizing of the slashed yarns was conducted in three steps as shown in Figure 4.5. The desizing conditions were the same in all three steps:

Temperature: 95 ^{o}C

Time: 8 minutes

Liquor Ratio: 15:1

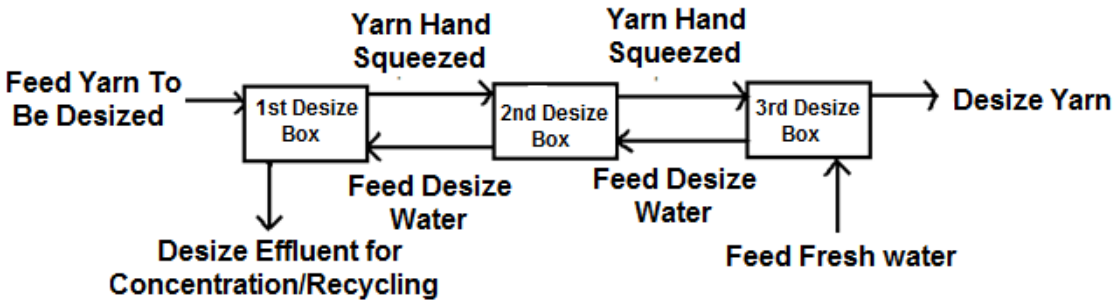


Figure 4.5: Line Diagram of Three-Step Desizing Process

Slashed yarn was first desized using the desize effluent stream obtained from the second desize box. The yarn was squeezed and the effluent stream was stored for size recovery. Squeezed yarn was desized again using the effluent stream obtained from the third desize box. Yarn was squeezed and the desized effluent was again stored to use in the first step. In the last step, squeezed yarn was desized again in fresh water and the effluent stream was kept for the second step. The wash water was topped-off with fresh water in the first and second steps.

4.3.5 Size Recovery

After discussions with the VFE manufacturer partner, VACOM, LLC, a Laborota 4000 G1 Rotary Evaporator was used for the fundamental studies instead of a true VFE unit, as the former is a good bench simulation of the full-scale industrial process (Section 4.2). The desize effluent stream was filtered through a sieve to remove solids (short fiber, dust and dirt) and stored in an oven at 90^{o}C. The desize effluent stream was concentrated at 65^{o}C using the rotary evaporator at constant vacuum. The desize effluent stream properties were not affected by storing at 90^{o}C, and the industry also stores PVA desize

effluent streams at this temperature. Recovered PVA size was used with or without added virgin PVA for the preparation of films and for subsequent-cycle slashing of yarns.

4.3.6 Size Formulation Viscosities with Impurities

Cotton chemical impurities were isolated from greige yarns as detailed earlier (Section 4.3.2). Size formulations were prepared as recommended by the E. I. DuPont Co. (Section 4.3.1). In preparing size formulations for recycle runs, a known quantity of cotton impurities was added instead of wax. Concentrations of all the solutions were kept constant. The final size formulations were kept stirred and air cooled to room temperature. The temperatures of all the samples were kept constant (27^{o}C). The solution viscosities were measured using a Brookfield Viscometer (Section 4.2).

4.3.7 Desizing Efficiency

Efficiency of the desizing process was checked by mass balance. A clean, empty glass beaker with aluminum foil was dried in an oven (~120^{o}C). The beaker was sealed with aluminum foil and weighed after cooling for 10 minutes. Total desize effluent stream was measured and water was evaporated from a known quantity of it, first by heating in the convection oven (~120^{o}C), and then fully drying the residuals in a vacuum oven. The beaker was then sealed with the aluminum foil and weighed again after cooling for 10 minutes. From the two beaker weights, the total solids content in the desize effluent stream was calculated. Theoretical and experimental values of solid content in the desize effluent stream were compared.

4.3.8 Slashed Yarn Add-On

The slashed yarn sheet consisted of 12 ends, and one meter of slashed yarn sheet was cut from 12 different places. Each pile and ground yarn sample thus contained 144 meters of yarn. Greige and slashed yarns weights were measured after being conditioned at 65% RH and 72^{o}F for 24 hours.

$$\text{Add} - \text{On } \% = \frac{\text{Weight of Slashed Yarn} - \text{Weight of Greige Yarn}}{\text{Weight of Greige Yarn}} * 100 \qquad \text{Eqn. (4.2)}$$

$$\text{Yarn Tex} = \frac{\text{Weight of the Yarn (g)}}{\text{Length of the Yarn (m)}} * 1000 \qquad \text{Eqn. (4.3)}$$

4.3.9 Recycled T-66 PVA Film Preparation and Testing

Films were cast from virgin and recycled T-66 PVA size using the Auto Draw III (Figure 4.6) device. The instrument included a glass plate and a coating rod. Approximately 15 ml of size solution was poured on the glass plate and spread mechanically with the help of the coating rod. The purpose of the coating rod was to lay a uniform layer of solution on the glass plate. The cast film was left overnight to air-dry, and then carefully removed from the glass plate by hand-peeling.

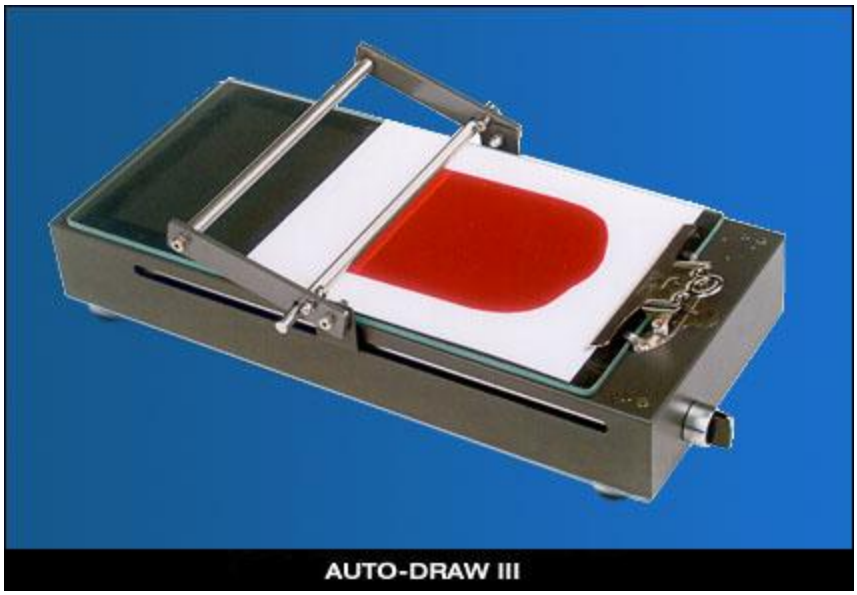


Figure 4.6: Auto-Draw III Film Casting Instrument [65]

4.3.9.1 Tensile Testing of Cast Films

Cast films were dried at 50^{o}C for two hours in a convection oven and then conditioned for 24 hours before testing at 65% relative humidity and 72^{o}F. Pure and recovered size films were tested for the tensile properties using ASTM Test Method D882-02 [66]. Samples of one cm width and five cm gauge length were prepared and tested for this study. Thickness of the samples was measured at four places using a micrometer. Breaking strength, breaking elongation and modulus of elasticity were calculated:

Breaking Strength

$$\text{Breaking Strength} = \frac{\text{Load at Break (N)}}{\text{Width of the Film (mm)} * \text{Thickness of the Film (mm)}} \quad \text{Eqn (4.4)}$$

Breaking Extension

$$\text{Breaking Extension} = \frac{\text{Elongation at Break (mm)}}{\text{Initial Length (mm)}} * 100 \qquad \text{Eqn. (4.5)}$$

Modulus of Elasticity

$$\text{Modulus of Elasticity} = \frac{\text{Strength}}{\text{Strain}} \qquad \text{Eqn. (4.6)}$$

4.3.9.2 Water Contact Angle on Cast Films

The contact angle of a distilled water droplet placed on the cast film was determined. VCA Optima instrument and VCA Optima XC software was used to measure the contact angle (Figure 4.7). A syringe of 100 micro liters was cleaned five times with distilled water. The syringe was filled with distilled water and placed back in the slot. The tip of the syringe was cleaned with paper towels and left to dry for 10-15 minutes. Drop size (0.3 micro liters), speed (high) and syringe size (100 micro liters) values were entered into the software. The contact angles of distilled water drops were measured at 10 places on the film, and the values averaged.

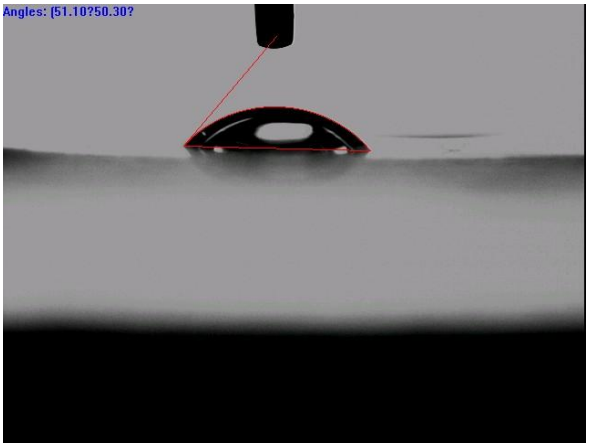


Figure 4.7: Distilled Water Drop on Recycled Size Film

4.3.10 Slashed Yarn Testing

Slashed yarns were dried in a convection oven at 50°C for two hours. The dried yarns were then conditioned for 24 hours at 65% RH and 72°F.

4.3.10.1 Tensile Testing

Greige and slashed yarns were tested for tensile properties using ASTM Test Method D2256-02 [67]. Samples of 10 cm gauge length were tested for tensile properties. Load at break, elongation at break, tenacity and work of rupture were obtained:

Tenacity at Break

$$\text{Tenacity at Break} = \frac{\text{Load at Break (N)}}{\text{Yarn Linear Density (Tex)}} \qquad \text{Eqn. (4.7)}$$

Breaking Extension

$$\text{Breaking Extension} = \frac{\text{Elongation at Break (mm)}}{\text{Initial Length (mm)}} * 100 \qquad \text{Eqn. (4.8)}$$

Work of Rupture

$$\text{Work of Rupture} = \text{Area under Load Elongation Curve (gf. cm)} \qquad \text{Eqn. (4.9)}$$

4.3.10.2 Yarn Hairiness

A Toray Fray Counter in S mode was used to determine the hairiness of the slashed yarns. Hairs of a spun yarn whose length was more than the set value were

counted. Hair length was set using a scale and dial. Ten samples of four meters each were taken from different places of the slashed yarn. Each sample was tested four times to achieve a valid representation of the hairs. Hairs were counted at different hair lengths and a graph was plotted of the numbers of hairs vs. hair length. Initially, the numbers of hairs increased with hair length, but after a critical hair length, the number of hairs began decreasing (Figure 4.8). This critical hair length was considered as a base line, i.e., true origin of hair length, and the number of hairs more than 1.5 and 2 mm hair length were counted. The number of hairs per meter was then calculated.

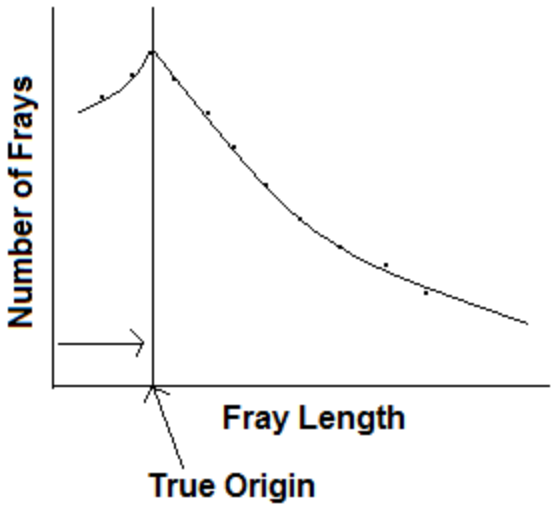


Figure 4.8: Number of Frays Plotted against Fray Length to Determine the Origin

4.3.10.3 Yarn Abrasion

Fifteen slashed yarns per test were abraded against square and round pins on the Ruti Webtester, and the number of abrasion cycles to first yarn breaks were recorded (Figure 4.9). Sixty samples of one yard length were tested. The experiment was

conducted at 500 abrasion cycles/minute. The tensioning device in the instrument was calibrated using a 10 N load. The total value of the tension was calculated and set using a two inch wide fabric. The tension employed with the yarn was 2.5-3.0 cN/tex. This value was multiplied by yarn tex and 15, as 15 yarn samples were mounted at a time. The set of 15 samples was repeated four times. The arithmetic mean of the number of abrasion cycles completed before first yarn break occurring in the four tests was calculated.

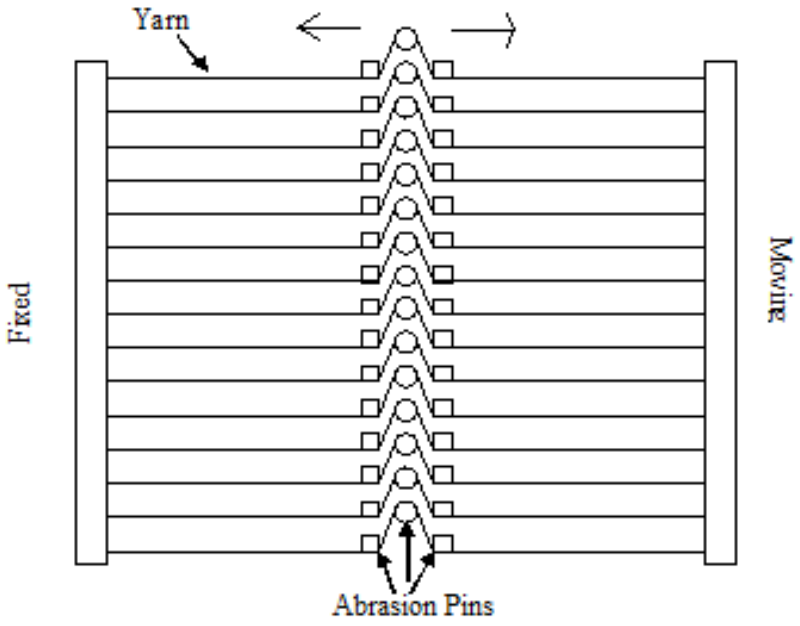


Figure 4.9: Line Diagram of Sulzer Ruti Webtester

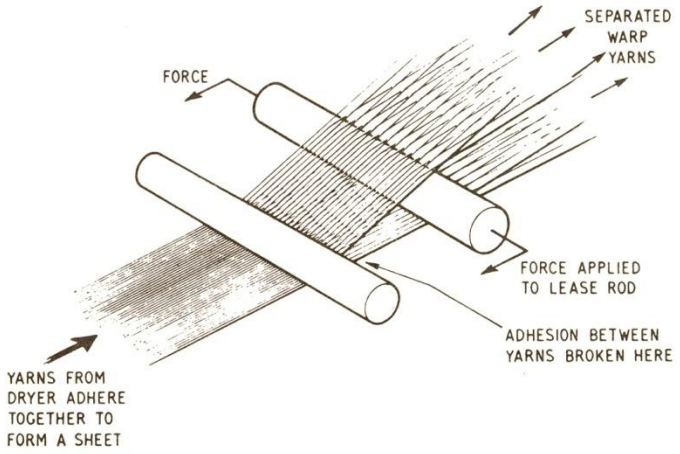
4.3.10.4 Bending Length

Yarn was laid on the FRL Cantilever Bending Length Tester and a slider was placed on top. The yarn was moved forward like a cantilever with the help of the slider.

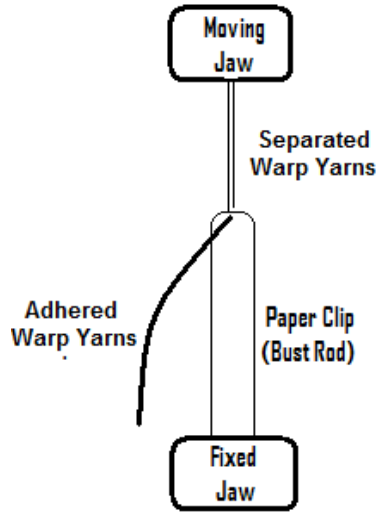
The slider was moved forward mechanically at a constant speed. The yarn hung like a cantilever as it moved forward at a constant rate until its hanging end bent under its own weight and touched a platform which was fixed at a constant angle (41.5^{o}) from the horizontal. The distance moved by the slider, i.e., hanging length of the yarn, was recorded. The average bending length of 25 samples was calculated.

4.3.10.5 Bust Rod Resistance

A typical yarn lease/bust rod system operating on a conventional slasher is shown in Figure 4.10a. The bust rod resistance of slashed yarns was measured on an Instron Model 5567 Tester. Two warp yarns adhered to each other by bridging size film were used for this experiment. Separated ends of the two warp yarns were held by the moving jaw of the Instron, whereas a metal paper clip used as the bust rod was held by the fixed jaw (Figure 4.10b). The other ends of the warp yarns adhering to each other were free. Resistance provided by the paper clip bust rod was measured by the load cell.



(a)



(b)

Figure 4.10: (a) Typical Leasing/Bust Rod System and (b) Diagram of Sample Mounting [24]

4.3.10.6 Size Diffusion

Diffusion of size across the yarn cross section was visually observed under a microscope. Samples of yarn cross sections were prepared by passing four ends of the sized yarn through a cork. The cork was cut perpendicular to its length with a sharp blade. Samples were observed under reflected light at 500 times magnification utilizing a LEICA DM IRM Microscope. Photographs were captured using Image Pro 6.2 software. The violet tracer dye was difficult to visualize even under 500X magnification, and thus the size diffusion in the yarn cross section images was difficult to determine. Matlab software was used to separate/enhance the color inside the yarn diameters using the software's "decorrstretch" command, allowing the size diffusion to be ascertained.

4.3.11 Thermogravimetric Analysis

The combined cotton chemical impurities/T-66 PVA mass in the desize effluent stream was measured using TGA. Samples were prepared by first evaporating the bulk water from the desize effluent stream (convection oven, ~120^{0}C, 4-5 hours) until dryness was achieved. Ash contents in the pure T-66 PVA size, in the cotton chemical impurities extracted from the greige yarns and in the isolated desize combined solids were determined at 650^{o}C using TGA. Samples were first heated to 120^{o}C at 10^{o}C per minute and then kept isothermal at 120^{o}C for 60 minutes to achieve dryness. The temperature was then raised to 650^{o}C at 10^{o}C per minute heating rate. Knowing the ash content of pure T-66 PVA and of the cotton chemical impurities extracted from the greige yarns, and determining the combined ash content of the desize effluent stream at 650^{o}C, the percentage by weight of impurities contained in the desize effluent stream was calculated (Appendix 1):

$$I\,\% = \frac{(\text{Ash \% in the Sample} - \text{Ash \% in the Elvanol T66})}{(\text{Ash \% in the Cotton Impurities} - \text{Ash \% in the Elvanol T66})} * 100 \qquad \text{Eqn. (4.10)}$$

$$I\% = \text{Impurity \% of Desize Effluent}$$

4.3.12 Intrinsic Viscosity of Size Formulations

Viscosity aids in estimating the average molecular weight of a polymer: the higher the molecular weight, the more viscous the polymer solution. Formulations from virgin T-66 PVA and recycled size were prepared at 0.4, 0.8, 1.2 and 1.6 g/dL concentrations, respectively. Recycled size formulations were prepared from the third slashing cycle of pile yarn. Solution viscosity was measured by the flow time taken by

the constant volume of water (solvent) and solution, as it was directly proportional to the flow time. Relative viscosity, $\eta_{r,}$ was the ratio of the viscosity of the polymer solution to the viscosity of the solvent at a given concentration [68]:

$$\eta_r = \frac{t}{t_0} \qquad \text{Eqn. (4.11)}$$

t = Flow time of solution

t_0 = Flow time of solvent

Specific viscosity, $\eta_{sp,}$ was the difference in the flow time of the polymer solution and the pure solvent, relative to the flow time of the pure solvent:

$$\eta_{sp} = \frac{t - t_0}{t_0} = \eta_r - 1 \qquad \text{Eqn. (4.12)}$$

Reduced viscosity $\eta_{red,}$ was the ratio of specific viscosity to the concentration of the solution:

$$\eta_{red} = \frac{\eta_{sp}}{c} \qquad \text{Eqn…..(4.13)}$$

c = Concentration of the solution

The plot between reduced viscosity on the ordinate and concentration on the abscissa gave a straight line with positive slope, i.e., followed the equation of a straight line in slope intercept form:

$$Y = b + mc \qquad \text{Eqn. (4.14)}$$

m: Slope of the line

b: Intercept on y axis

c: Concentration

The empirical equation relating molecular weight to the viscosity was by Huggins [68]:

$$\eta_{red} = [\eta] + k_H[\eta]^2 c \qquad \text{Eqn. (4.15)}$$

$[\eta]$ = Intrinsic viscosity

k_H = Huggins constant

From equation 4.14 and 4.15, $k_H[\eta]^2$ was m, the slope of the line, and $[\eta]$ was b, the y-intercept. Inherent viscosity, η_{inh} , was the ratio of the natural logarithm of the relative viscosity to the concentration of the polymer solution:

$$\eta_{inh} = \frac{\ln(\eta_r)}{c} \qquad \text{Eqn. (4.16)}$$

A plot between inherent viscosity on the ordinate and polymer concentration on the abscissa was a straight line with negative slope. The empirical equation relating molecular weight to the viscosity was by Kraemer [68]:

$$\eta_{inh} = [\eta] + k_A[\eta]^2 c \qquad \text{Eqn. (4.17)}$$

k_A = Kraemer constant

From equation 4.14 and 4.17, $k_A[\eta]^2$ was the slope of the line where as $[\eta]$ was the intercept of the line. From a plot of both methods together, the two lines meeting at their common intercept provided the intrinsic viscosity. Finally, the polymer molecular weight was calculated using $[\eta]$ and the Mark-Houwink Equation:

$$[\eta] = KM^{\alpha} \qquad \text{Eqn. (4.18)}$$

K, α = Constants

M = Viscosity-average molecular weight

4.3.13 Desized Yarn Color

Samples were made by wrapping desized yarns under slight tension and touching each other on a piece of cardboard to produce a fabric-like flat surface. The Hunter MiniScan (MS/S-4000L) Reflectometer was first standardized using a white tile. The reflectometer was then placed on the sample and CIE ΔL, Δa, Δb and ΔE values were recorded [69]. A positive value of ΔL indicates that the sample (desized yarn) is lighter than the standard, whereas a negative value indicates it is darker than the standard. A positive value of Δa indicates that the sample is redder than the standard, whereas a negative value dictates that the sample is greener than the standard. Similarly, a positive value of Δb shows that the sample is yellower than the standard, and a negative value indicates that the sample is bluer than the standard. The total color variation of the sample

from the standard is given by the overall color difference, ΔE, which is calculated in the CIE formula from the three input parameters, ΔL, Δa and Δb.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 VFE Evaporation Process

In the case of UF concentration of a desize effluent stream, a semi-permeable membrane excludes the high molecular weight PVA, whereas low molecular weight PVA, water and some cotton chemical impurities permeate through it. The loss of the low molecular weight PVA "tail" of the distribution changes the properties of the recovered PVA film. In the case of VFE, water is evaporated under vacuum at low temperatures, and thus all extracted cotton impurities, water and PVA remain in the concentrate. The PVA film properties are modified because of the addition of cotton impurities. In VFE, the desize stream water is evaporated and then condensed to generate pure, hot water, which enjoys unrestricted reuse as make-up water in the plant's many wet processes. The energy required in the VFE process to generate steam is thus an approximate trade-off with plant boiler energy that would normally go to generate the hot water required by the plant. Water recovered in the UF process as permeate contains low molecular weight PVA and cotton impurities, which restricts its use in the plant. In VFE, no polymeric spiral-wound film membrane exists to foul or degrade, and no high pump pressures are required to overcome pressure differentials across the membrane, thus lowering electrical costs. No effluent is discharged from the VFE process. Pure, condensed hot water is recovered and reused in the plant (up to 70% of the desize effluent feed stream in the case of towel manufacturing), and ~30% of the water remains with the

PVA and cotton impurities in the concentrate. Up to 90% of the total thermal input energy to the VFE process is recovered [1]. An increase in apparent size mass recovery occurs with VFE over UF, as the recovered size in the former contains all of the desized PVA MW distribution as well as the extracted cotton chemical impurities.

5.2 Yarn Impurities

Griege cotton yarns used in both the towel pile and ground constructions were tested for impurity levels (Section 4.3.2). Impurities extracted from both yarns under the optimized desizing process conditions (two-step method, Section 4.3.4.1) constituted ~2.3% of the yarn masses.

5.3 Effects of Cotton Chemical Impurities on Recycled T-66 PVA Films and Slashed Yarns

To study the effect of cotton chemical impurities on the physical properties of recycled size films and yarns, wax was not used in these experiments. Size formulations were developed at 0%, 14.3%, 25%, 33.3% and 40% w/w impurities concentrations.

5.3.1 Tensile Properties of Recycled T-66 PVA Films

5.3.1.1 Breaking Strength

Samples were prepared and tested on the Instron Model 5567 Tester using ASTM Test Method D 882-02. The breaking strength of the simulated, recycled T-66 PVA size film decreased with an increase in cotton chemical impurities level (Figure 5.1). The decrease in breaking strength was due to the low molecular weight cotton chemical impurities which were occluded in the recycled size. Upon increasing the concentration

of cotton chemical impurities in the recycled size, the strengths of the blend films continued to decrease (Figure 5.1).

In conventional slashing, wax is added to the T-66 PVA to decrease the strength and increase the flexibility of the blended film. With the added cotton chemical impurities, less or no wax was projected to be added to the recovered size, similar to the earlier UF studies where wax was not added to the recycled PVA size formulations [12, 32, 48, 49], because the impurities perform the same functions in the blend film as the wax, e.g., lower the film strength and add toughness, lubricity and flexibility. All of the impurity-added traits to the recycled size film improve subsequent weave ability.

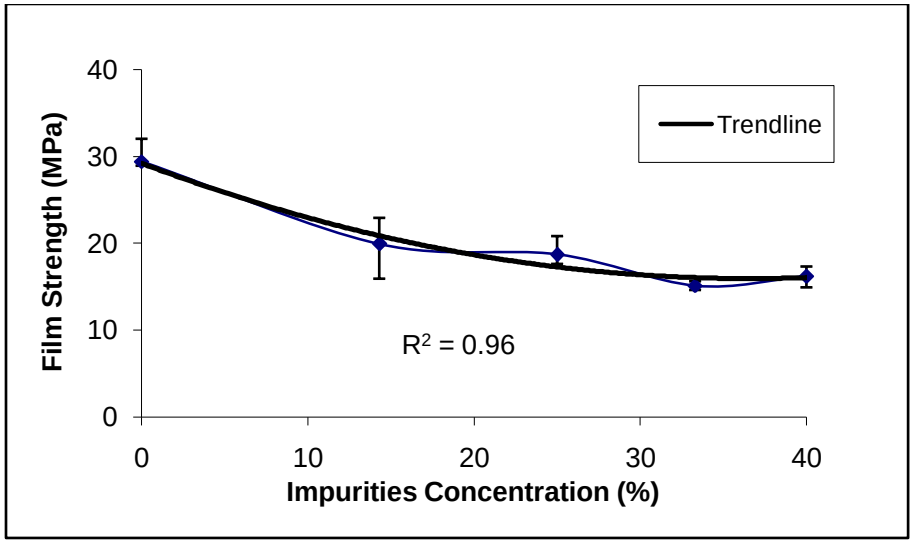


Figure 5.1: Changes in Strength of Recycled T-66 PVA Films with Impurities Concentration

5.3.1.2 Elongation at Break

Elongation at break of recycled T-66 PVA size film initially decreased with an increase in cotton chemical impurities, but at an impurity level of 15% w/w, it began to

increase (Figure 5.2). The increase in elongation at break was due to slippage of the T-66 PVA molecular chains, which was enhanced because of the presence of the low molecular weight impurities. Studies showed that films of recovered size isolated by the rotary evaporator, which simulates the VFE process, exhibited improved elongation at break performance over virgin PVA films. An increase in elongation at break avoids the cracking of size film on the slashed yarn surface and keeps it smooth. Smooth surfaces reduce the friction among yarns and between yarns and weaving machine parts, such as drop wires and heddles, thereby reducing the number of warp yarn breakages.

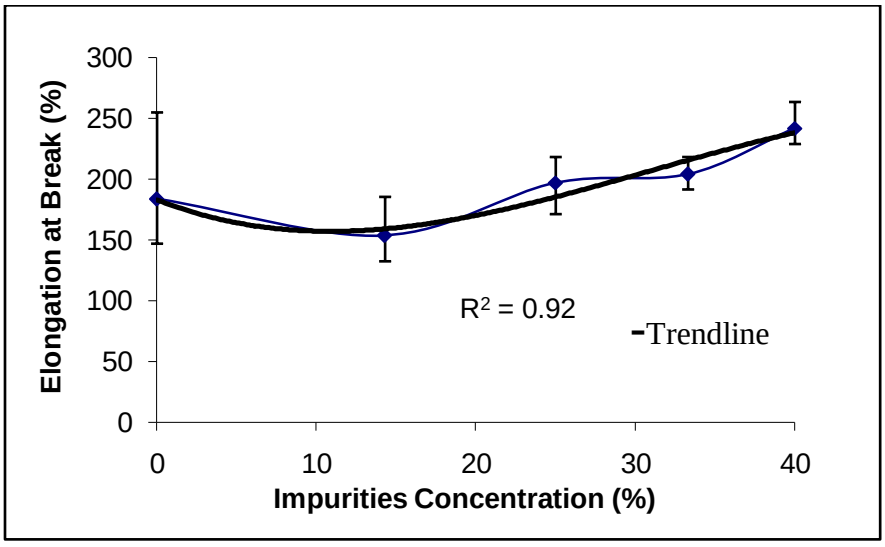


Figure 5.2: Changes in Elongation at Break of Recycled T-66 PVA Films with Impurities Concentration

5.3.1.3 Modulus of Elasticity

In towel weaving, all-PVA size is normally not used in slashing pile yarns. PVA-slashed yarns are stiff in nature and difficult to form into loops. Recycled T-66 PVA size

showed a decrease in modulus of elasticity (<80%) with an increase in impurity levels (Figure 5.3). Both an increase in elongation at break and a decrease in load at break of the film contributed to the decrease in modulus of elasticity. A decrease in modulus of elasticity facilitates pile loop formation from slashed yarns [70].

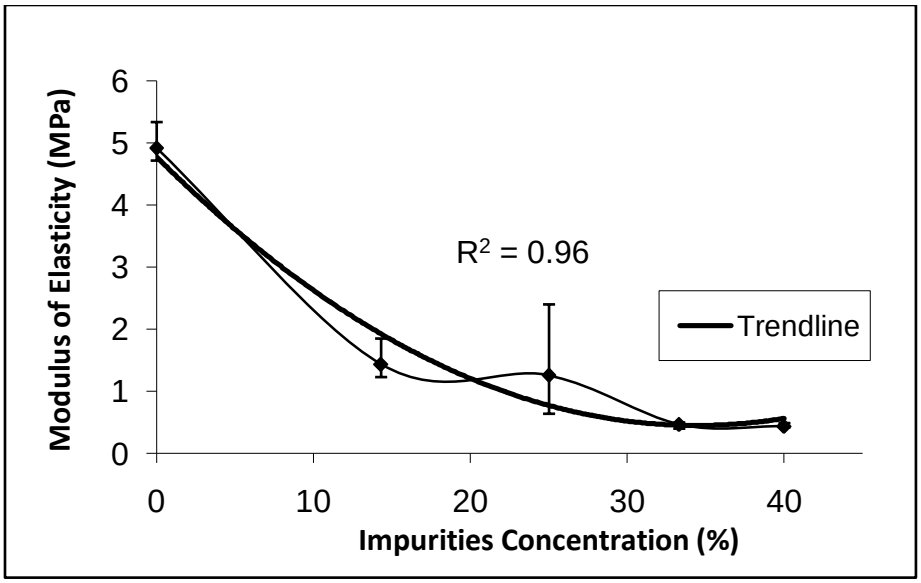


Figure 5.3: Changes in Modulus of Elasticity of Recycled T-66 PVA Films with Impurities Concentration

5.3.2 Wet Ability

Approximately 95% of size is removed from formed fabrics during desizing. The contact angle of the water droplet on recycled T-66 PVA film decreased with increases in impurities levels (Figure 5.4). An increase in PVA size film hydrophilic properties facilitates its wetting in desizing, aiding removal.

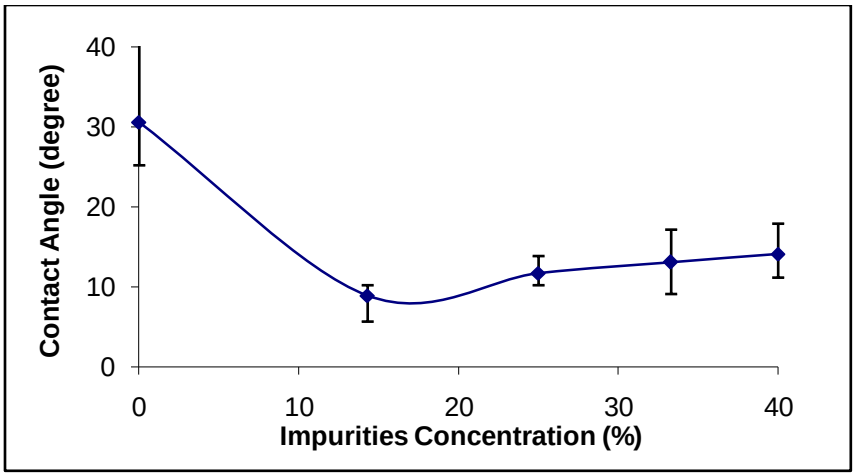


Figure 5.4: Changes in Contact Angle of Water Droplets on Recycled T-66 PVA Size Films with Impurities Concentration

5.3.3 Viscosity

Industry controls the slashing process with the viscosity/concentration of the size solution. Size add-on decreases with increase in viscosity up to a minimum, but very high viscosities increase the size add-on (Figure 5.5). Figure 5.5 shows size formulation viscosities in the ~5-30 cP range give similar pick-ups. Low size formulation viscosity is required for effective slashing [71]. To decrease the viscosity at a given concentration, the temperature of the size formulation must be increased. The viscosities of recycled T-66 PVA size formulations decreased with increased cotton chemical impurity concentrations, allowing slashing at a relatively low size box temperature (70^{o}C, Figure 5.6). Figure 5.6 was plotted at a constant 5% w/w size formulation concentration.

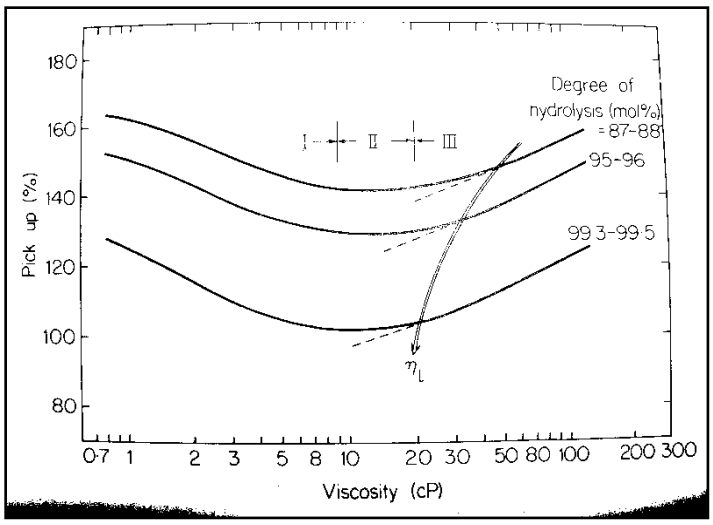


Figure 5.5: Pick-Up vs. Viscosity of PVA Solution [30]

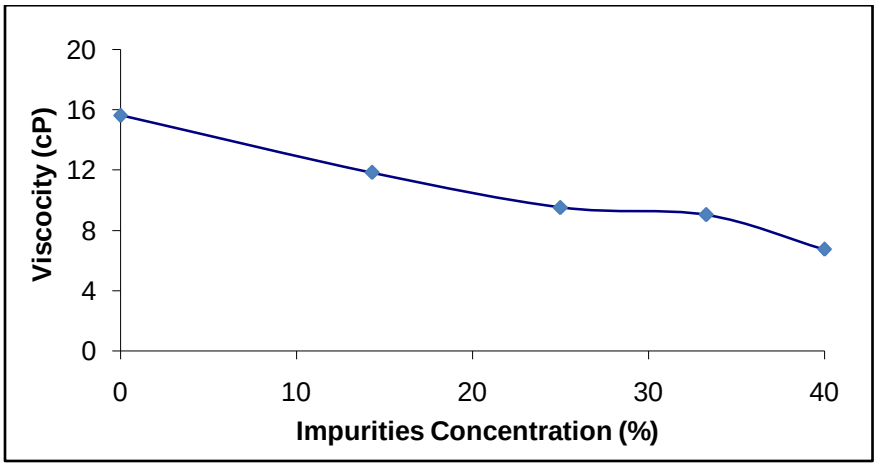


Figure 5.6: Changes in Viscosities of Recycled T-66 PVA Size Formulations at Constant Concentration (5% w/w) with Impurities Concentration

5.3.4 Tensile Properties of Slashed Yarns

5.3.4.1 Yarn Tenacity

The tenacity of yarns slashed with recycled T-66 PVA initially decreased, but after the 15% cotton chemical impurities level was reached, it remained nearly constant

with increased impurity levels (Figure 5.7). When wax is added to the size formulation in all-PVA slashing, the yarn tenacity is also decreased. Figure 5.1 shows that the recycled T-66 PVA film strength decreased with an increase in impurities concentration, but the blend recycled size better penetrated the yarn and thus increased the yarn strength. As a result, little change occurred in the tenacity of the yarn slashed with the recycled T-66 PVA size formulations with increasing cotton chemical impurities content in the film.

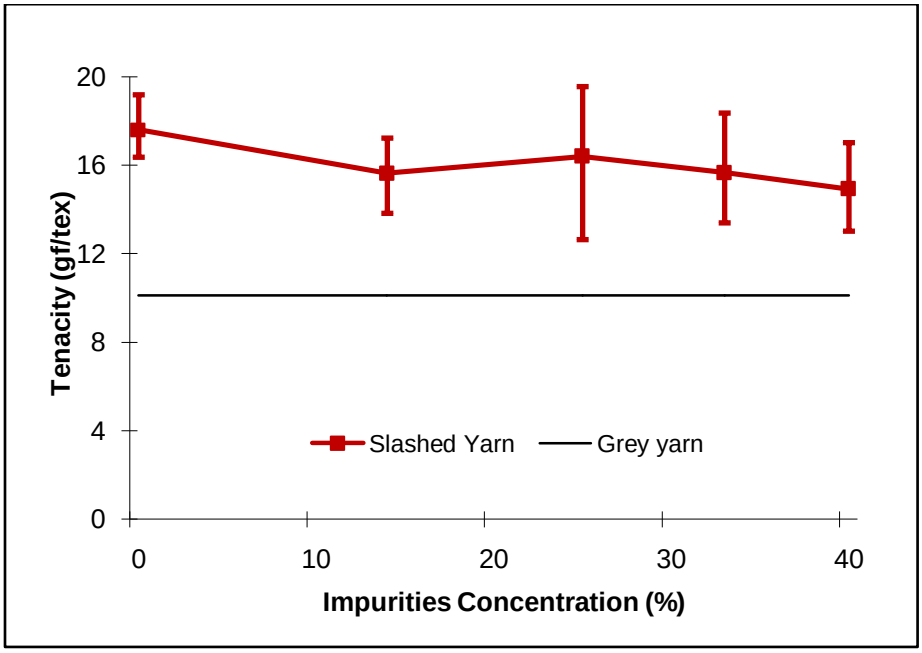


Figure 5.7: Changes in Yarn Tenacity at Break of Recycled T-66 PVA Slashed Yarn vs. Impurities Concentration in the Size Film

5.3.4.2 Work of Rupture

Work of rupture of the slashed yarns initially decreased with an increase in impurities, but became nearly constant after the 15% w/w impurities level was reached (Figure 5.8). Addition of wax also reduced the work of rupture, as it reduced the load at

break of the slashed yarn, but further increases in cotton chemical impurities maintained the work of rupture level, as impurity-contaminated size penetrated deeper inside the yarn.

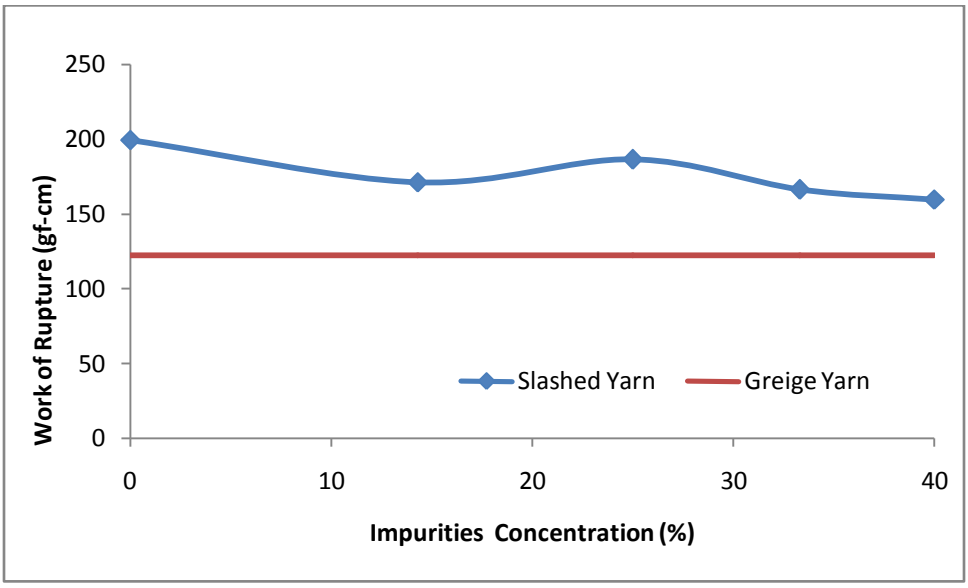


Figure 5.8: Yarn Work of Rupture of Recycled T-66 PVA Slashed Yarn with Impurities Concentration in the Size Formulation

5.3.5 Bust Rod Resistance

The bust rod resistance of slashed yarn initially increased with an increase in impurities concentration, but after 15% size add-on, it decreased (Figure 5.9). The low molecular weight cotton chemical impurities in the recycled T-66 PVA size thus decreased the strength of the bridging film between the slashed yarns.

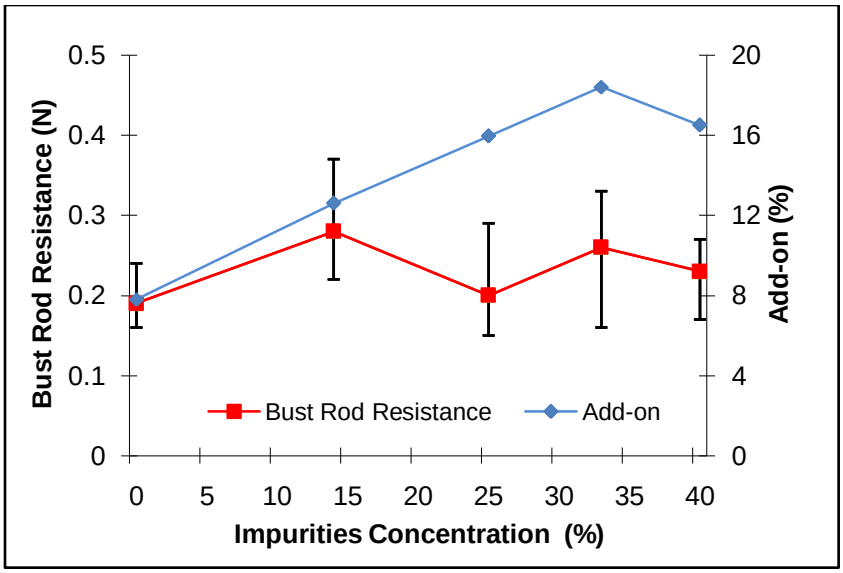


Figure 5.9: Bust Rod Resistance and Size Add-On of Recycled T-66 PVA Slashed Yarn with Impurities Concentrations in the Size Formulation

5.3.6 Summary of the Effects of Occluded Cotton Chemical Impurities on Recycled T-66 PVA Films and Slashed Yarns

In VFE, recycled size entrains extracted yarn impurities (~2.3% of yarn weight per desizing cycle). The apparent molecular weight average of the recycled size decreased, as the cotton chemical impurities were lower in molecular weight than the polymeric T-66 PVA. The breaking strength of the recycled size films decreased with increasing impurities concentration, and the addition of wax to T-66 PVA size formulations also decreased the film strength. With the occluded cotton impurities present, little or no wax was added to the recovered size in subsequent development of the technology. Elongation at break of the recycled size film increased with impurities concentration, while the modulus of elasticity decreased. The viscosity of the recycled size film decreased with impurities concentration. The contact angle of a water droplet on the recycled size film decreased with increasing impurities concentration, indicating

increased wet ability and ease of removal in desizing. Bust rod resistance initially increased, but at higher impurities concentrations in subsequent cycles, it decreased. Slashed yarn tenacity and work of rupture slightly decreased on initial size recycle sequences, but remained constant on further increases of impurities concentrations in subsequent cycles.

5.4 Effects of Wax, Cotton Chemical Impurities and their Combinations on Recycled T-66 PVA Films and Slashed Yarns

Experiments were designed at four levels of wax and four levels of impurities as shown in Table 3.2. Ground yarns were slashed with simulated formulations devised by mixing known quantities of wax, T-66 PVA and cotton chemical impurities (~15% solids pickup). Sixteen samples of ground yarn were produced using the two-end bench slasher (Section 4.2), and films were made from recycled size at all 16 combinations of wax and cotton chemical impurity percentages (Table 3.2). Films were tested for tensile strength and elongation at break, whereas slashed yarns were tested for tenacity, work of rupture, bust rod resistance, size add-on, hairiness and abrasion resistance.

5.4.1 Tensile Properties of Recycled T-66 PVA Films

5.4.1.1 Breaking Strength

Sixteen samples of simulated, recycled T-66 PVA films were tested on the Instron Model 5567 Tester using ASTM Test Method D 882-02. The breaking strength of the recycled T-66 PVA size film showed a decreasing trend with increases in wax percentages at different impurities levels, but after 8% of PVA mass wax level, further

increases in wax in the size formulations had little impact on the film breaking strengths (Figure 5.10). A similar trend was found when impurities percentage was increased at different wax percentage levels (Figure 5.11). After the 25% of total solids impurities concentration level was reached, further increases in impurities had little impact on the breaking strength of recycled T-66 PVA films. In essence, impurities acted like wax in modifying the film properties. In conventional slashing, approximately 8% of wax is added to the virgin PVA. With occluded cotton impurities present in the recycled T-66 PVA films, wax additions to the recycled size formulations was concluded to be unnecessary.

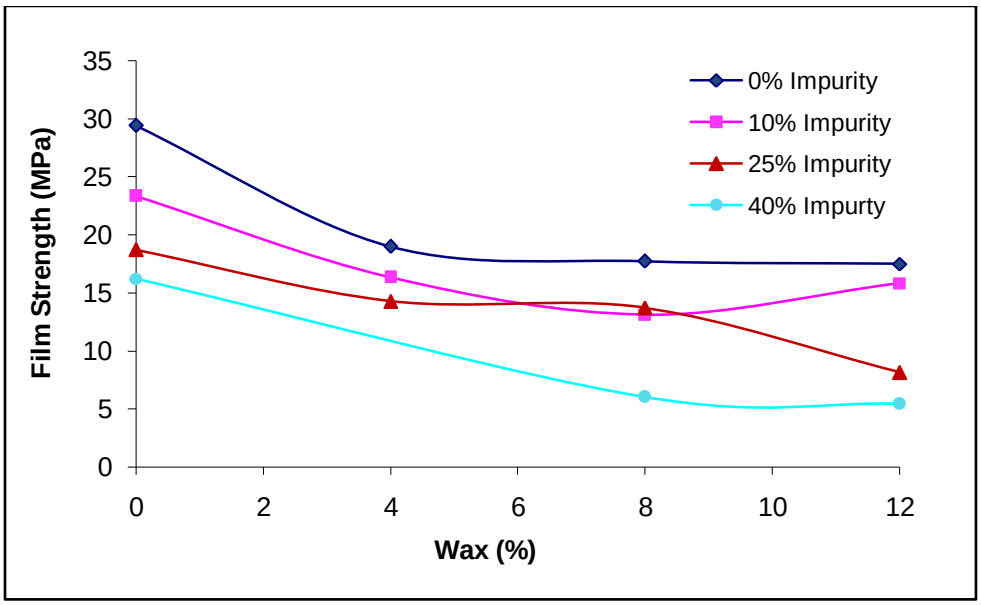


Figure 5.10: Changes in Strength of Recycled T-66 PVA Films vs. Wax Percentage at Different Impurities Concentration in the Size Formulation

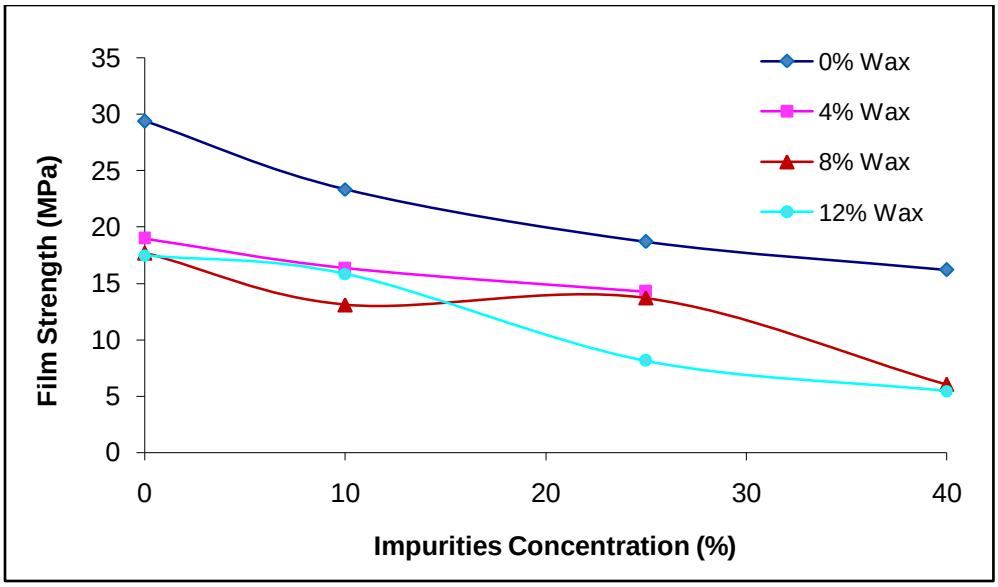


Figure 5.11: Changes in Strength of Recycled T-66 PVA Films vs. Impurities Concentration at Different Wax Percentage in the Size Formulation

5.4.1.2 Elongation at Break

A decrease in elongation at break of the recycled T-66 PVA size films occurred at different impurity levels with an increase in wax percentage (Figure 5.12). At 0% wax level, elongation at break increased with impurities, i.e., the cotton chemical impurities acted as a PVA plasticizer, mimicking the wax performance (Figure 5.13). Elongation at break of recycled T-66 PVA film initially increased with an increase in impurity percentage at different wax percentage levels, but on further increases in impurities concentration, film elongations at break decreased, except at 0 % wax level. A shift in the film elongation to break peak towards lower impurities percentage occurred as the wax percentage level increased, i.e., as the wax percentage increased, its effects became more prominent.

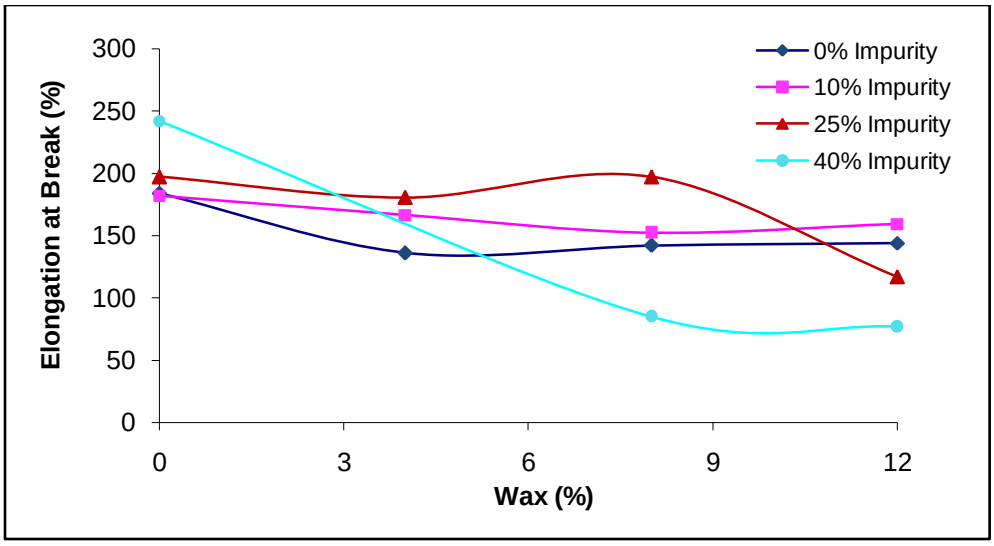


Figure 5.12: Changes in Elongation at Break of Recycled T-66 PVA Films vs. Wax Percentages at Different Impurities Concentration in Size Formulations

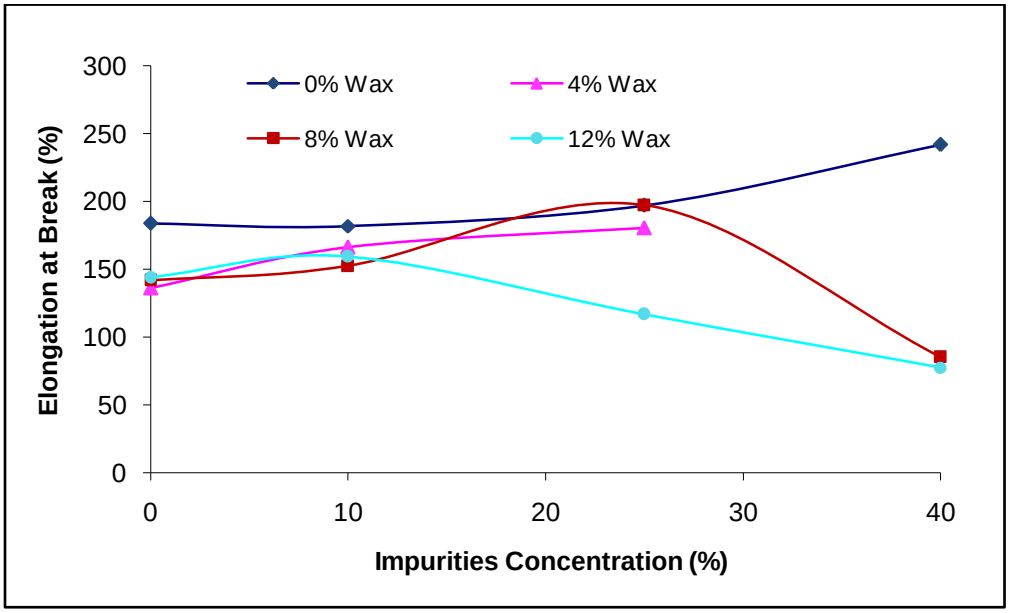


Figure 5.13: Changes in Elongation at Break of Recycled T-66 PVA Films vs. Impurities Concentration at Different Wax Percentage in the Size Formulations

5.4.2 Tensile Properties of Slashed Yarns

5.4.2.1 Tenacity at Break

Slashed yarn samples were prepared and tested on the Instron Model 5567 Tester using ASTM Test Method D2256-02. The tenacity of slashed yarns with respect to cotton chemical impurities concentrations are shown in Figure 5.14. The tenacity initially decreased with an increase in impurity percentage at 0% wax level, but on increasing the impurities concentrations beyond 15% of total solids, the tenacity was nearly constant.

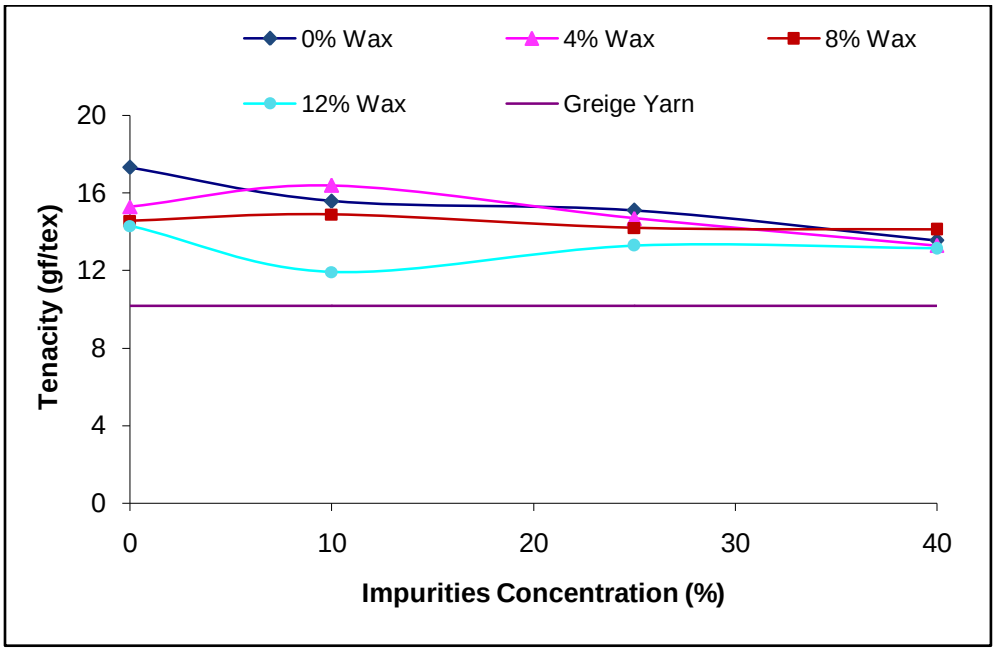


Figure 5.14: Changes in Yarn Tenacity at Break of Recycled T-66 PVA Slashed Yarn vs. Impurities Concentration at Different Wax Percentage in the Size Formulations

A similar trend was observed with an increase in wax percentage at 0% impurities level, but the yarn tenacity was nearly constant when the wax percentage was greater than 8% of PVA (Figure 5.15). Other tenacity curves also showed similar trends, but with

some variability, as the greige ground yarn itself exhibited some variability in tenacity. With an increase in either wax or impurities in the size formulation, the T-66 PVA percentage decreased in the resulting film, which caused a corresponding decrease in overall yarn tenacity. Cotton chemical impurities are of relatively low molecular weight, and their occlusion in a recycled PVA size formulation decreases the viscosity and thus enhances size penetration into the yarn diameter. Slashed yarn, together with the added impurities/PVA, becomes a composite structure, which aids in maintaining the tenacity. After slashing, yarn loads at break should increase by 20% compared to greige yarn, i.e., tenacity should increase by 20% [27, 64]. Although yarn slashed with recycled T-66 PVA size formulations containing the cotton chemical impurities showed a decrease in tenacity, the latter still remained 20% greater than that of the corresponding greige yarn. Similar trends were observed with wax addition to the PVA film. The observations confirmed the earlier conclusion that impurities perform like wax in the PVA film, and can thus effectively substitute for wax in the recycled size formulations.

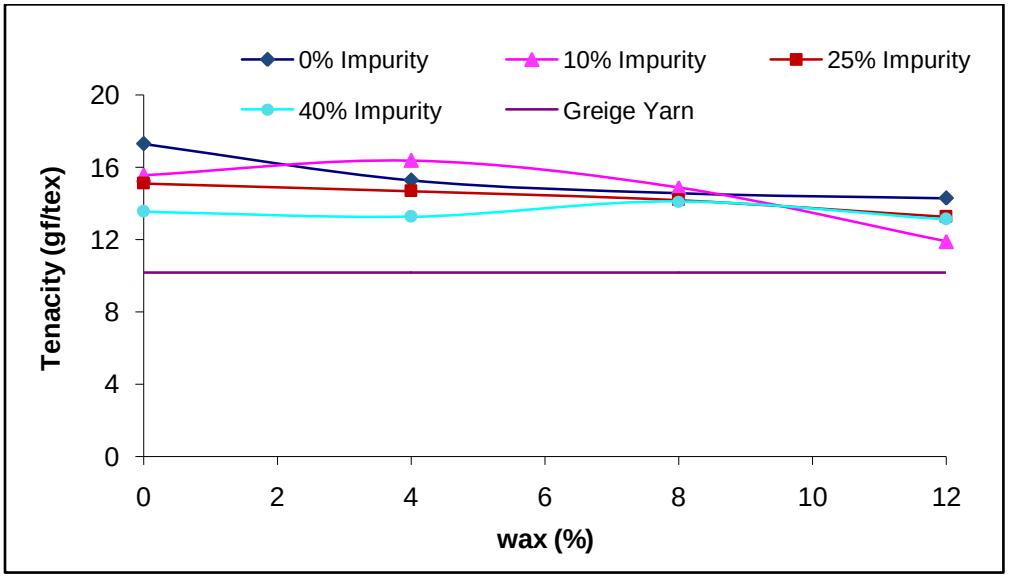


Figure 5.15: Changes in Yarn Tenacity at Break of Recycled T-66 PVA Slashed Yarn vs. Wax Percentage at Different Impurities Concentration in the Size Formulations

5.4.2.2 Work of Rupture

As the slashed warp yarns undergo repeated cycles of stress and strain in weaving, the energy/work required to break the yarn is critical, i.e., work of rupture. Slashed yarn load at break should increase 20% compared to the greige yarn, but at the cost of reducing its elongation at break. Elongation at break should not be reduced below 20% of the greige yarn after slashing [27, 64]. Work of rupture was calculated as the area under the load vs. elongation curve. By extension, the work of rupture of the slashed yarn should approximate that of the corresponding greige yarn. Figure 5.16 shows that the slashed yarn work of rupture at 0% wax level initially decreased, but remained nearly constant after 25% impurities concentration level was reached.

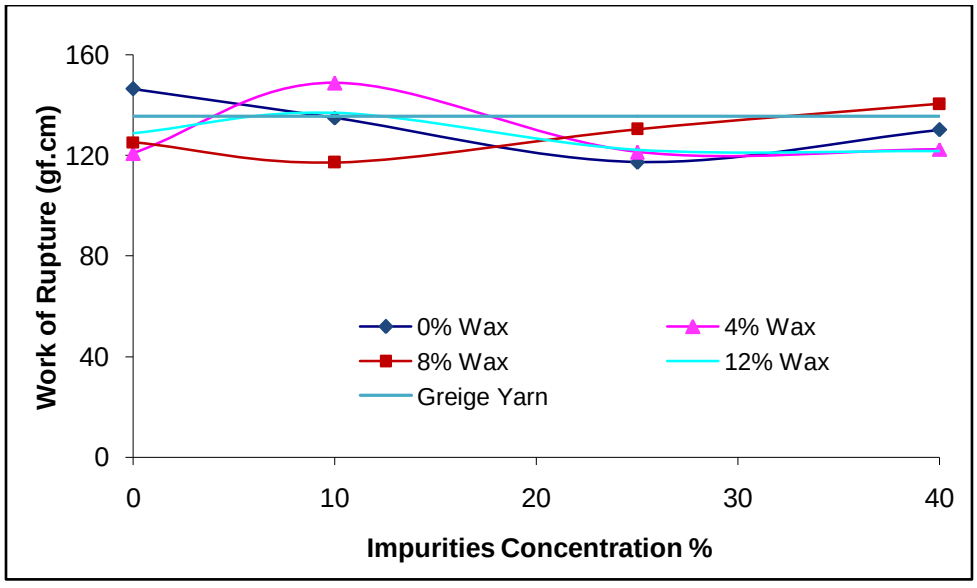


Figure 5.16: Changes in Recycled T-66 PVA Slashed Yarn Work of Rupture vs. Impurities Concentration at Different Wax Percentage in the Size Formulation

At other wax percentage levels, the work of rupture initially showed some variation, but approached a plateau after the 25% impurities concentration level was reached. Work of rupture showed similar behavior with an increase in wax percentage at 0% impurities concentration, but other curves exhibited some variability, as in the case of increasing impurities concentration at constant wax concentration. In all cases, the slashed yarn work of rupture approximated that of the corresponding greige yarn (Figure 5.17).

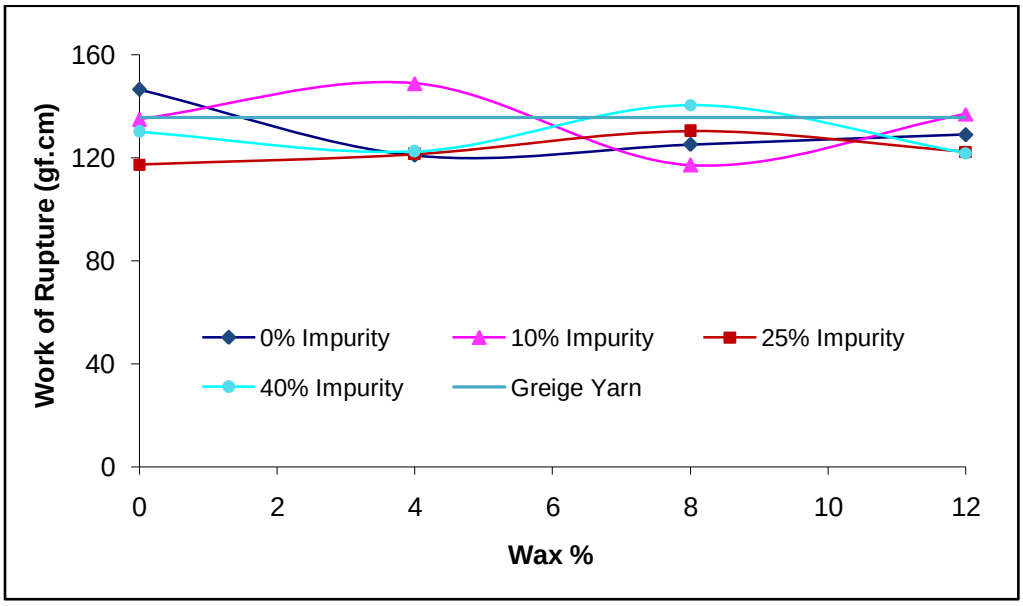


Figure 5.17: Changes in Recycled T-66 PVA Slashed Yarn Work of Rupture vs. Wax Percentage at Different Impurities Concentration in the Size Formulation

5.4.2.3 Slashed Yarn Hairiness

The number of fibers of length greater than a defined length protruding out of the yarn body was measured as hairiness. Hairs were counted using the Toray Fray Counter (Section 4.3.10.2). Slashed yarn hairs of length more than 2 mm and 1.5 mm were

counted as recommended by the instrument manufacturer. The number of 2 mm and 1.5 mm hairs decreased considerably compared to the greige yarn after slashing with all combination of wax and impurity percentages (Figures 5.18-5.21). The same ground yarn slashed by Springs Industries, using the conventional slashing formulation ((PVA T-25+Elastech 2002)/Starch/Wax: (41+15)/35/9), was also compared with the recycled T-66 PVA slashed yarn.

Figures 5.18-5.21 confirmed a considerable decrease in hairiness of all slashed yarns compared to the greige ground yarn. The decrease in hairiness was due to size film formed on the surface of the warp yarns during slashing, i.e., in essence, the surface hairs were "glued" to the yarn body. All the combinations of wax and impurity percentages resulted in reduced slashed yarn hairiness below or near that of the Spring Industries slashed yarn, indicating that the performance of the recycled T-66 PVA size film at the bust rods of slashing was comparable to that of the Springs Industries size formulation film.

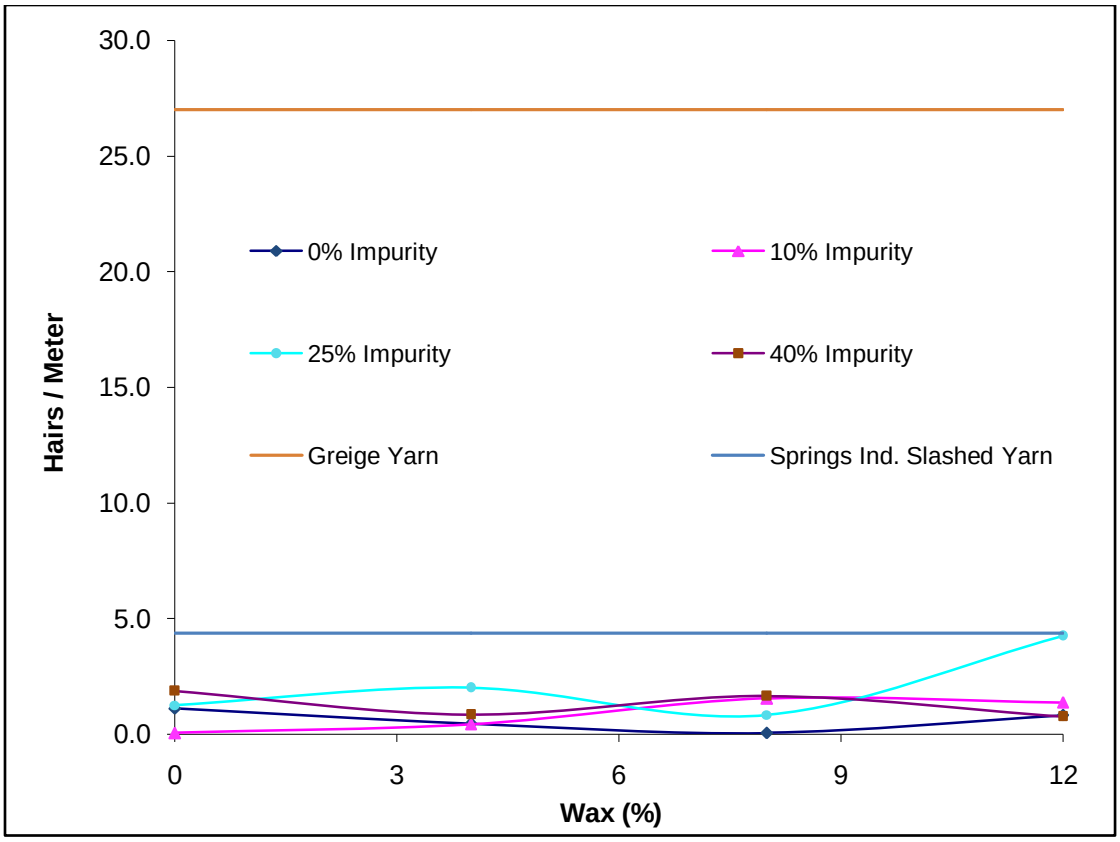


Figure 5.18: Changes in Recycled T-66 PVA Slashed Yarn Hairiness (2 mm) vs. Wax Percentage at Different Impurities Concentration in the Size Formulation

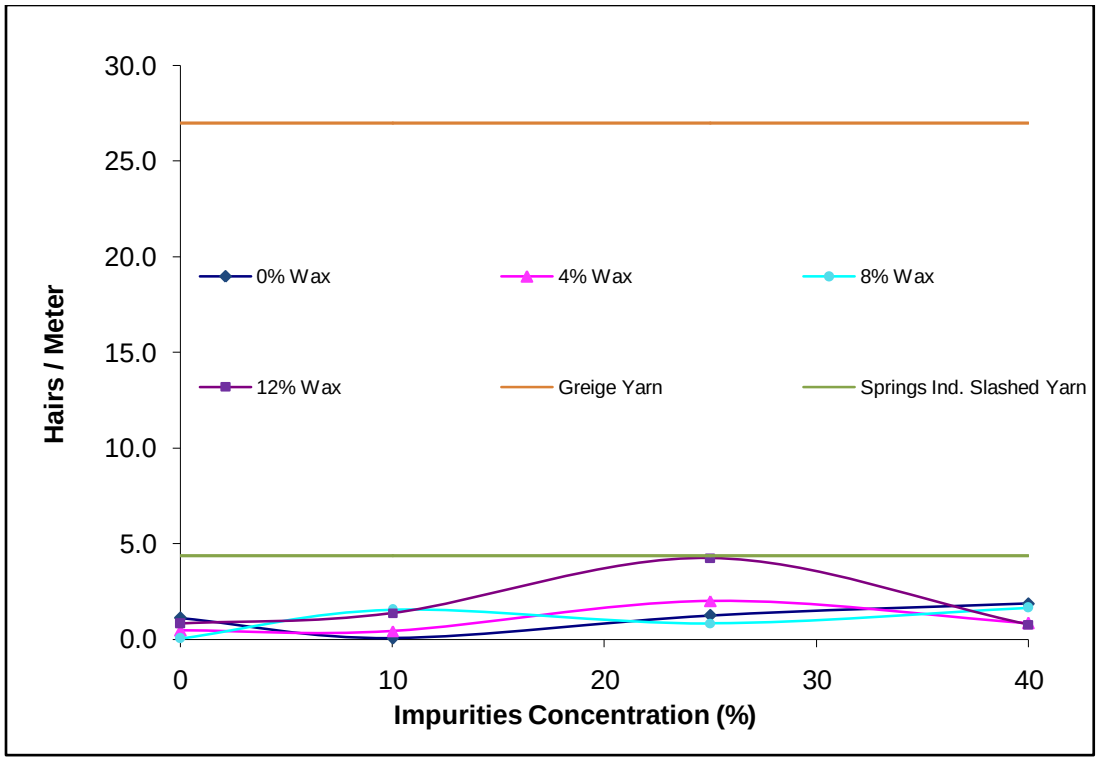


Figure 5.19: Changes in Recycled T-66 PVA Slashed Yarn Hairiness (2 mm) vs. Impurities Concentration at Different Wax Percentage in the Size Formulation

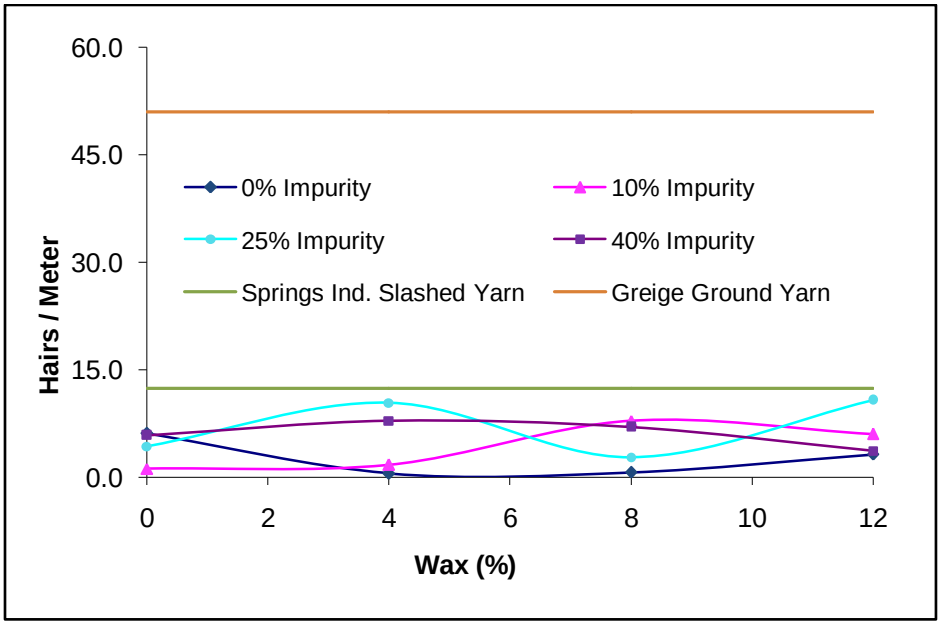


Figure 5.20: Changes in Recycled T-66 PVA Slashed Yarn Hairiness (1.5 mm) vs. Wax Percentage at Different Impurities Concentration in the Size Formulation

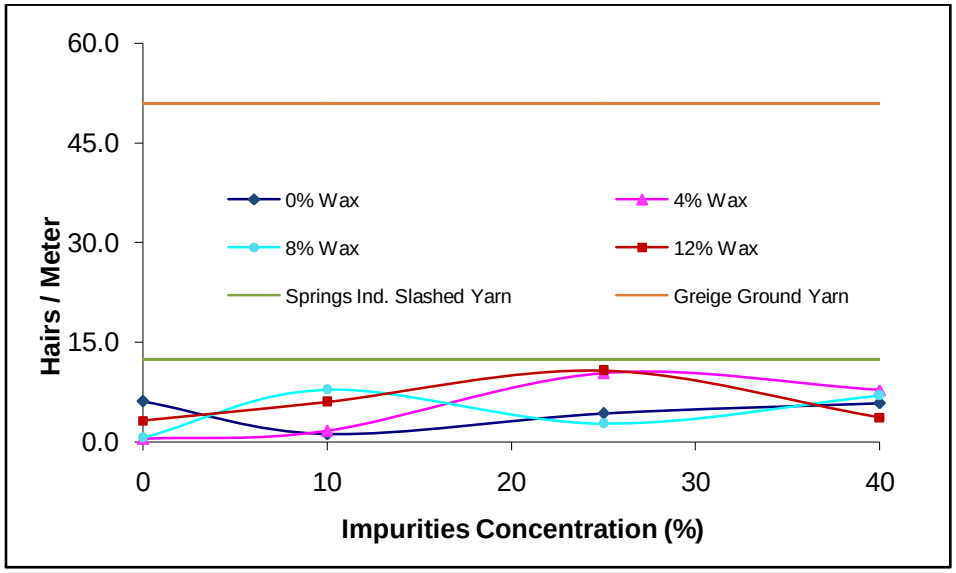


Figure 5.21: Changes in Recycled T-66 PVA Slashed Yarn Hairiness (1.5 mm) vs. Impurities Concentration at Different Wax Levels in the Size Formulation

Figures 5.22 and 5.23 show that at 0% wax with increase in impurities concentration and 0% impurity with increase in wax percentage level with increase in impurity and wax percentage, respectively, slashed yarn hairiness first decreased and then increased. Initially, the simulated recycled size formulations contained an elevated percentage of T-66 PVA and formed a thick, high-strength film located mainly on the yarn surface. Impurities were of lower molecular weight than T-66 PVA, and as their percentage increased and the size formulation viscosity correspondingly decreased, more size penetration into the yarn occurred, resulting in an albeit weaker, but substantially thinner, cured film on the surface. The overall result was increased yarn hairiness at the higher wax or impurities concentration levels in the film.

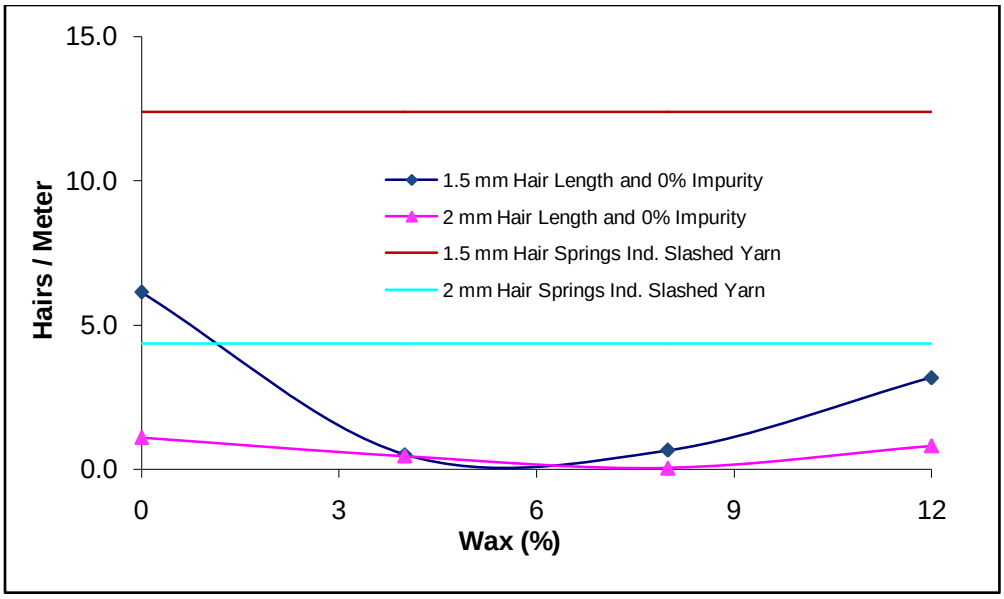


Figure 5.22: Changes in Recycled T-66 PVA Slashed Yarn Hairiness with Wax Percentage at Zero Percent Impurity Concentration in the Size Formulation

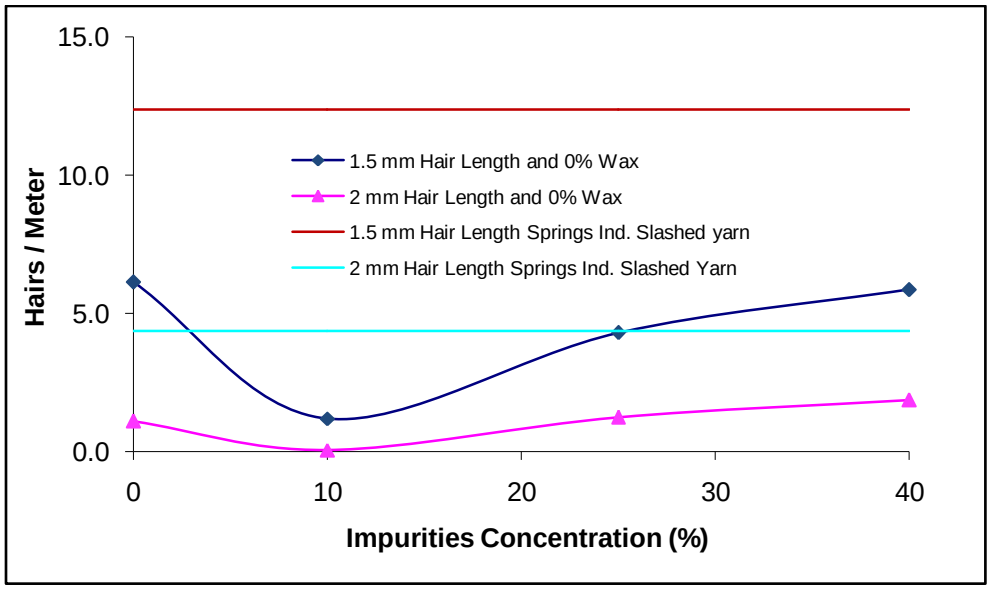


Figure 5.23: Changes in Recycled T-66 PVA Slashed Yarn Hairiness vs. Impurity Concentration at Zero Percent Wax in the Size Formulation

5.4.2.4 Bust Rod Resistance

After drying the slashed yarns on steam cans and thus forming/curing the size film, the warp is in a sheet form, i.e.,yarns are attached to neighboring yarns by bridged films. The bust rod separates the yarns by breaking the bridged films, and in this process, yarns sometimes break and short fibers (hairs) are always pulled out of the separated staple yarns. Excessive hairiness creates problems in air jet weaving, as the warp yarns are close to each other in space, and protruding hairs can disrupt the air flows emitting from booster jets positioned across the lay of the loom. At 0% impurity level in the T-66 PVA/varying percentages of wax size formulations, bust rod resistance increased, but on increasing the wax percentage above 8% on mass of PVA, bust rod resistance decreased (Figure 5.24). A decrease in resistance was directly due to the wax concentration increase in the film, as it reduced film strength. A similar effect was observed at 0% wax level with an increase in impurities concentration up to 15% (Figure 5.25). When the impurities concentration surpassed 15%, the bust rod resistance decreased. Other combinations of impurities and wax in the recycled size resulted in decreased slashed yarn bust rod resistance because of a corresponding decrease in film tear strength (Appendix 1).

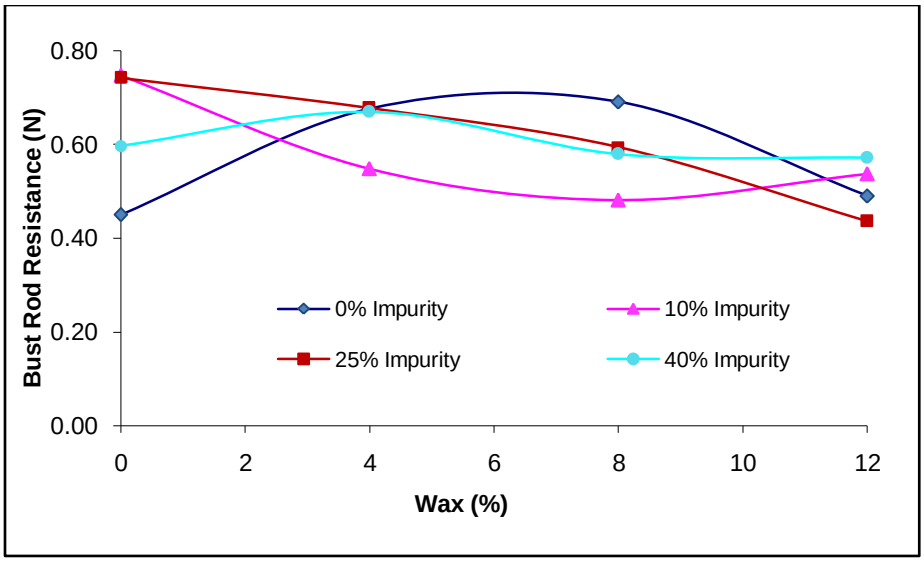


Figure 5.24: Bust Rod Resistance of Recycled T-66 PVA Slashed Yarn vs. Wax Percentage at Different Impurities Concentration in the Size Formulation

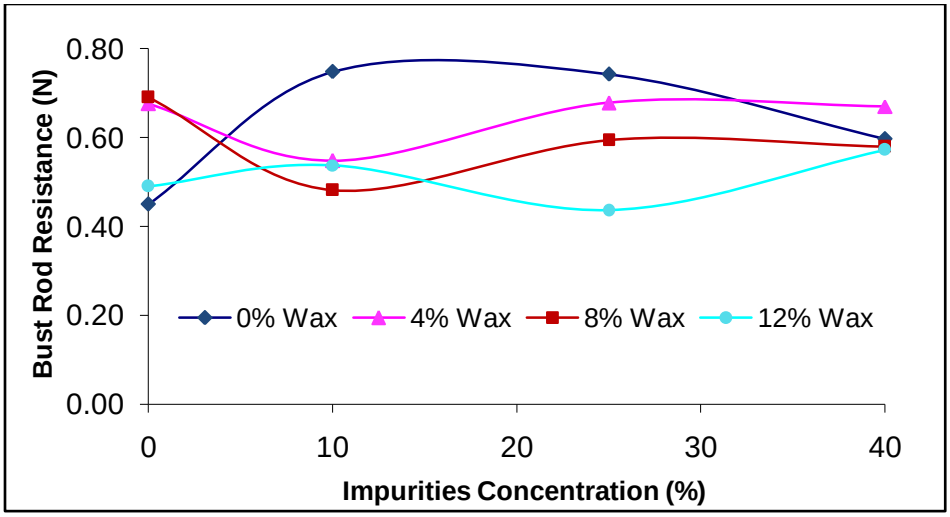


Figure 5.25: Bust Rod Resistance of Recycled T-66 PVA Slashed Yarn vs. Impurities Concentration at Different Wax Percentage in the Size Formulation

5.4.2.5 Abrasion Cycles to First Yarn Breaks

In weaving, warp yarns undergo repeated cycles of abrasion with various machine parts. The Ruti Webtester provides a simulation of the weaving process and tests this

critical property, i.e., the number of abrasion cycles of 15 slashed yarns to achieve a first break (Section 4.3.10.3). Slashed yarn samples were tested as recommended by the Webtester manufacturer. Fifteen samples were mounted at a time and experiments were repeated four times. Figures 5.26 and 5.27 show the average abrasion cycles to first yarn breaks in four experiments. The numbers of abrasion cycles to first yarn breaks initially showed increasing trends with an increases in impurities and wax concentrations in the simulated recycled PVA formulations. With slashed yarn, both wax and cotton impurities reduce friction by increasing surface lubricity, and thus increase the number of abrasion cycles required to achieve first yarn breaks. On further increases in impurities and wax concentrations, however, the numbers of abrasion cycles to first yarn breaks decreased due to the corresponding decreased T-66 PVA percentages in the recycled size formulations. A decrease in polymeric T-66 PVA reduced the film thickness on the yarn surface, whereas increasing low molecular weight impurities/wax concentrations facilitate penetration of the size formulations inside of the yarn diameters and away from the abrading surface. Higher wax and impurities concentrations thus decreased the number of abrasion cycles to first yarn failures, but the values were always greater than or equal to those achieved with the Springs Industries slashed yarn on the Ruti Webtester® , and much greater than those of the corresponding greige yarn.

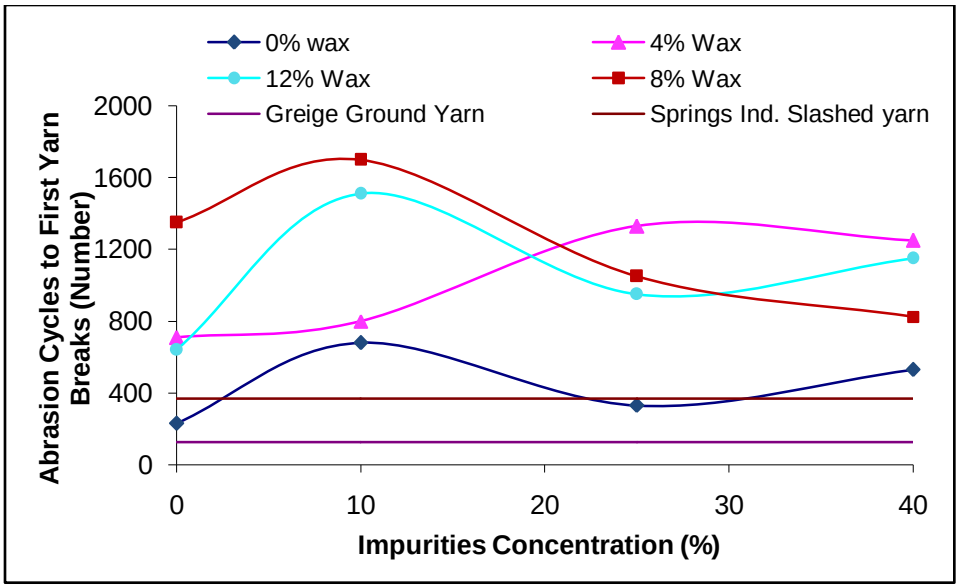


Figure 5.26: Number of Abrasion Cycles to First Yarn Breaks of Recycled T-66 PVA Slashed Yarn vs. Impurities Concentration at Different Wax Percentage in the Size Formulation

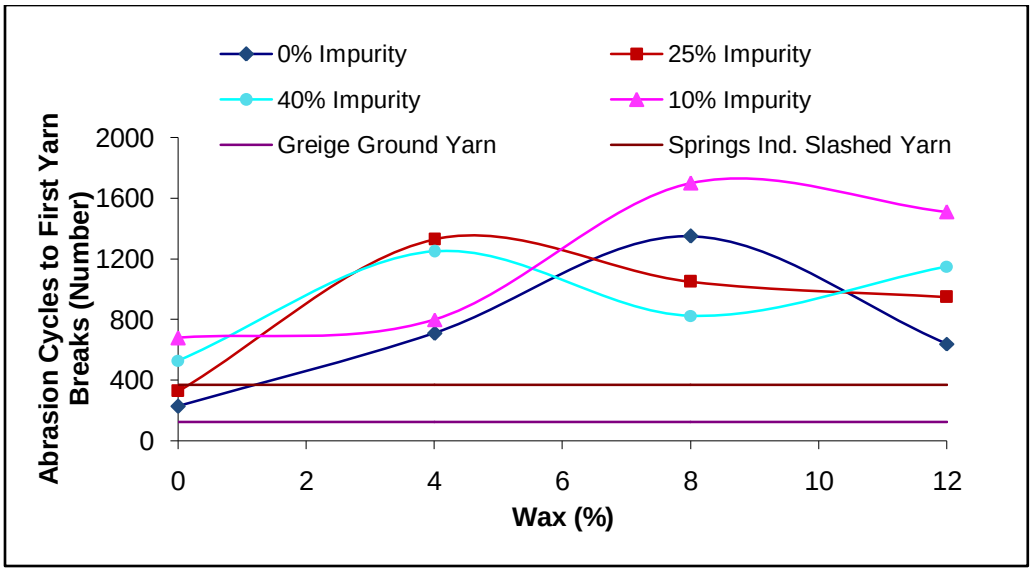


Figure 5.27: Number of Abrasion Cycles to First Yarn Breaks of Recycled T-66 PVA Slashed Yarn vs. Wax Percentage at Different Impurities Concentration in the Size Formulation

5.4.2.6 Summary of Effects of Wax, Cotton Chemical Impurities and their Combinations on Recycled T-66 PVA Films and Slashed Yarns

Cotton chemical impurities acted like wax in the simulated, recycled T-66 PVA size films and resultant recycled size slashed yarns, with mechanical properties of the latter similar or improved compared to those of Springs Industries' conventional slashed yarn. Recycled T-66 PVA slashed yarn experiments were conducted with up to 40% impurities concentration and compared to Spring Industries slashed yarn. To determine the break-even point of the impurities concentration in the size film to maintain required slashed yarn properties, experiments were next extended up to 100% impurities at 0% wax level in the simulated, recycled size formulations.

5.5 Effects of up to 100% Cotton Chemical Impurities on the Properties of Recycled Size Slashed Yarns

Slashing experiments were conducted on ground yarn constructions at 55%, 75% and 100% impurities concentrations in the size formulations. The simulated recycled size formulations were prepared as detailed earlier (Section 4.3.1.1).

5.5.1 Yarn Tenacity

The tenacity of the recycled size slashed yarn initially decreased, but for impurities concentrations greater than 40%, it was nearly constant (Figure 5.28). The observed recycled size slashed yarn tenacity was higher than that of slashed yarn provided by Springs Industries at any percentage of impurities in the formulation. The yarn tenacity results revealed that the 100% level of impurities size formulation, i.e., the one containing no T-66 PVA, yielded slashed yarn with a tenacity >20% higher than that

of the greige yarn, but changes in other physical properties of the recycled size slashed yarn were as important as yarn tenacity in predicting weave ability, e.g., abrasion resistance.

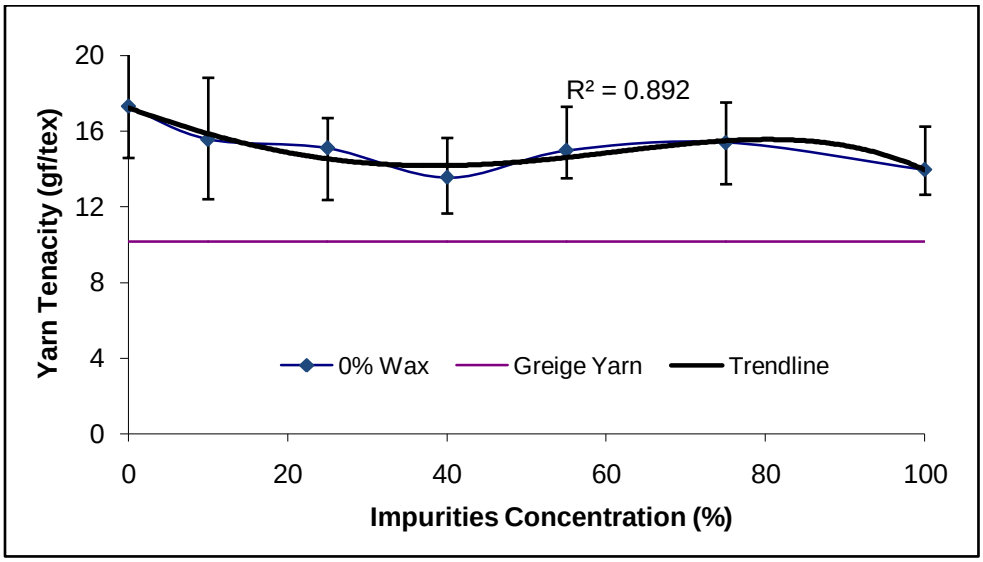


Figure 5.28: Tenacity at Break of Recycled Size Slashed Yarn vs. Impurities Concentration in the Size Formulation

5.5.2 Yarn Work of Rupture

The work of rupture of the simulated recycled size slashed yarns initially decreased, but after 25% of impurities concentration was reached in the formulation, it increased (Figure 5.29). The work of rupture achieved was greater than or equal to the recommended value from industry, i.e., comparable to that of the greige yarn.

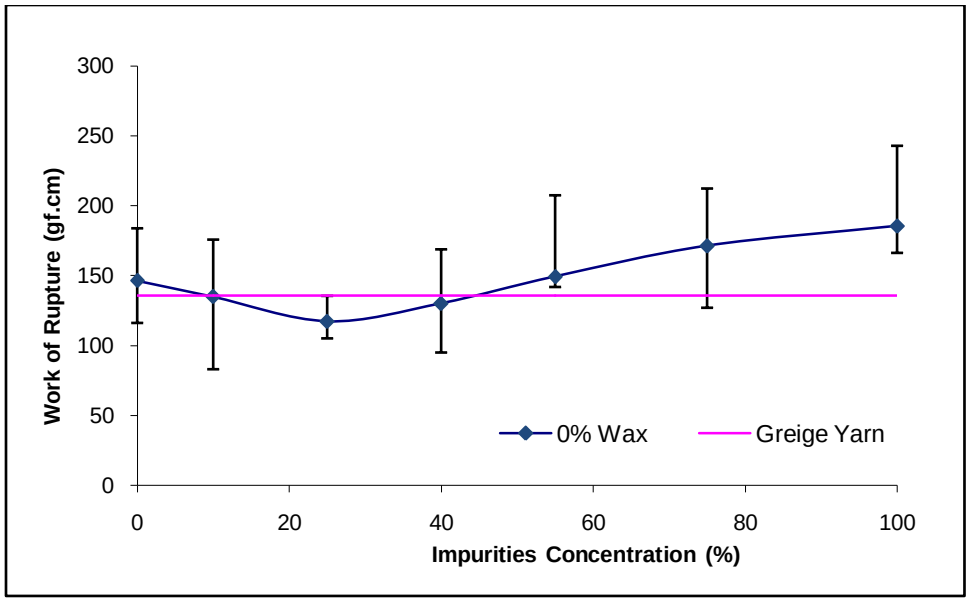


Figure 5.29: Work of Rupture of Recycled T-66 PVA Slashed Yarn vs. Impurities Concentration in the Size Formulation

5.5.3 Yarn Hairiness

Simulated recycled slashed yarn hairiness (hairs with length greater than 1.5 mm and 2 mm) was quantified in Figure 30. The hairiness initially decreased, but after 10% impurity level was reached, it increased. The percentage numbers of hairs more than 1.5 mm and 2 mm length was greater than that of the Springs Industries slashed yarn when the cotton chemical impurities concentration exceeded 60% in the size formulation. As detailed earlier, more size penetration inside the yarn with the higher impurities concentration formulations (and conversely lower T-66 PVA concentrations) resulted in a thinner layer of size on the yarn surface, leading to increased hairiness (Section 5.4.2.3).

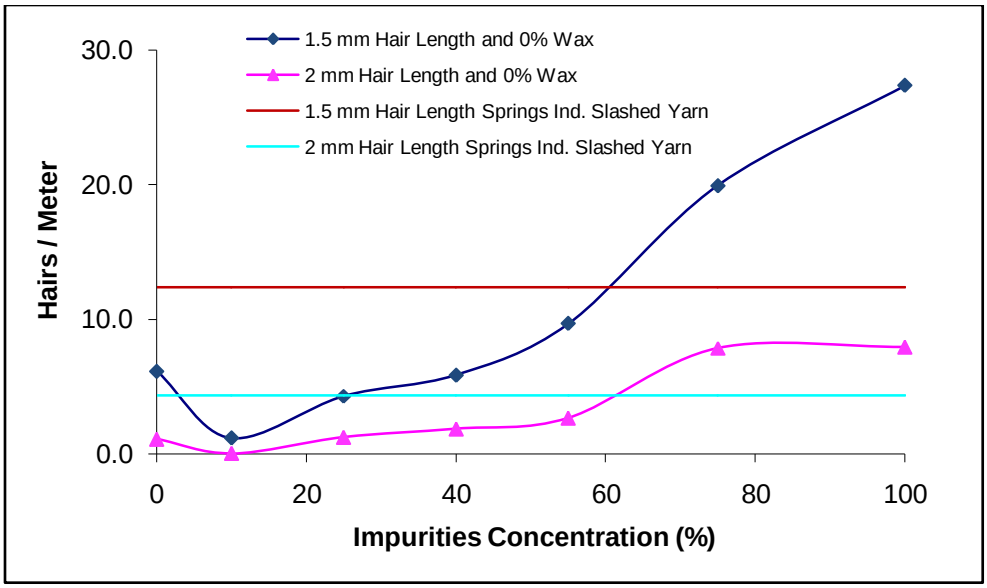


Figure 5.30: Changes in Recycled T-66 PVA Slashed Yarn Hairiness vs. Impurities Concentration in the Size Formulation

5.5.4 Bust Rod Resistance

As the impurities concentration increased in the formulation, the simulated recycled size film strength also decreased, making it easier for the bust rod to tear the size film bridging the yarns and thus separating them. Figure 5.31 shows that after an initial increase in bust rod resistance at lower impurities concentration, it decreased with increasing impurities concentration and approached zero resistance level at 100%. Film tearing load also showed the similar trend. Film tearing load initially increased because T-66 film were crystalline and brittle and tear at low load with addition of impurities film became soft and required more load to tear. Addition of impurities decreased the film strength and hence impurities more than 25% decrease the film tearing load (Appendix 1).

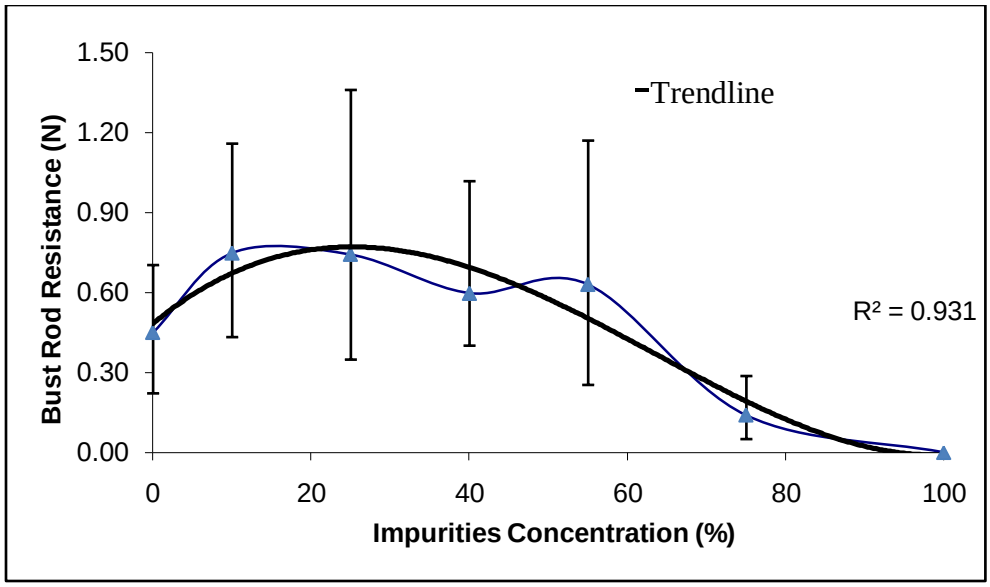


Figure 5.31: Bust Rod Resistance of Recycled T-66 PVA Slashed Yarn vs. Impurities Concentration in the Size Formulation

5.5.5 Yarn Abrasion Cycles

The number of abrasion cycles to first yarn breaks of the simulated recycled size slashed yarns on the Ruti Webtester initially increased as the cotton chemical impurities concentration increased, as the impurities in the yarn surface film decreased the friction between the yarn and the metal rods of the instrument (Figure 5.32). However, the number of abrasion cycles to first yarn break decreased beyond 10% impurities concentration, as the higher percentage of impurities decreased the film strength (Section 5.3.1.1). The numbers of abrasion cycles achieved to first yarn breaks were greater than or equal to the number achieved with the Spring Industries slashed yarn up to 60% impurities concentration, but when the latter was exceeded 60%, the numbers of abrasion cycles to first yarn breaks decreased, falling below that of the Spring Industries slashed

yarn standard. At 100% impurities concentration in the size formulation, the numbers of abrasion cycles to first yarn breaks were the same as those achieved with greige yarn.

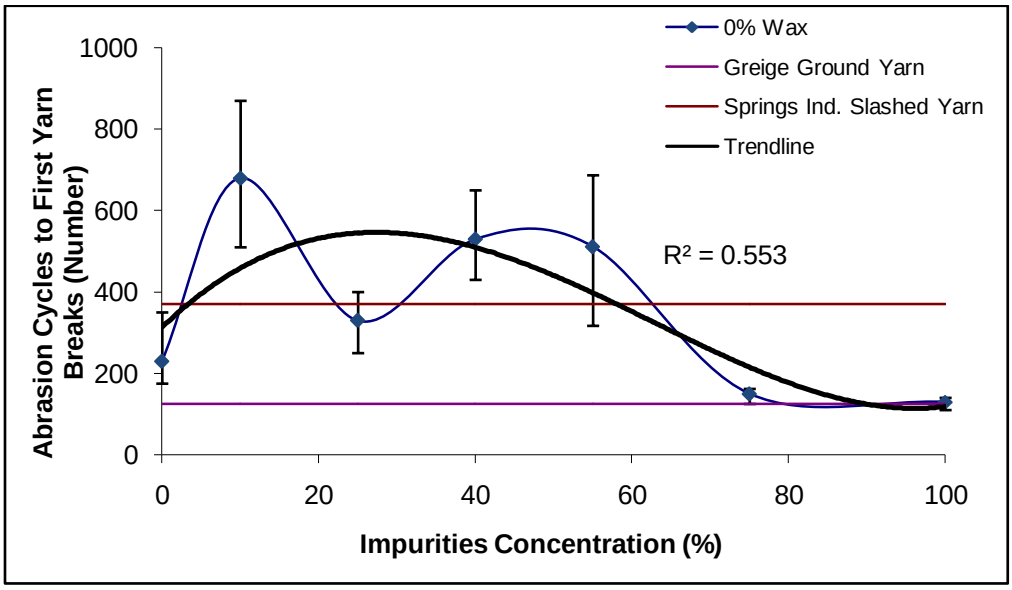


Figure 5.32: Number of Abrasion Cycles to First Yarn Breaks of Recycled T-66 PVA Slashed Yarn vs. Impurities Concentration Levels in the Size Formulation

5.5.6 Summary of Effects of up to 100% Cotton Chemical Impurities on Simulated Recycled Size Slashed Yarns

Table 5.1 summarizes the results of the extended research of increasing impurities concentration in the simulated recycled size. The simulated recycled size slashed yarn properties showed that tenacity, work of rupture and bust rod resistance were acceptable up to a 100% impurity level, whereas degree of hairiness and abrasion resistance above 60% impurities concentration were below those of the Springs Industries conventional slashed yarn, and essentially approaching those of greige yarn.

Table 5.1: Summary of Simulated Recycled Size Slashed Yarn Properties vs. Impurities Concentration Compared to Springs Industries Conventional Slashed Yarn

Impurity Levels (%) →	10	20	30	40	50	60	70	80	90	10
Slashed Yarn Tenacity										
Work of Rupture										
Bust Rod Resistance										
Hairiness (1.5 mm)										
Hairiness (2 mm)										
Abrasion Cycles to First Yarn Break										

5.6 Proof of Concept Scale-Up Trials Utilizing Webtex® Pilot Slasher

Using the bench scale results and in consultation with the industrial partners, the maximum cotton chemical impurities concentrations in the recycled T-66 PVA size for both pile and ground yarns were optimized for weave ability. The optimized, maximum allowable concentration of impurities in the recycled T-66 PVA size formulation for towel pile yarns was determined to be 60% (Table 5.1), whereas with ground yarns, the value was concluded to be 45%. Towel ground yarns undergo excessive stress, strain, abrasion, etc., as they traverse moving parts of the weaving machine, and thus require a higher size solids add-on (10% by yarn weight) than pile yarn (3%, see Appendix 3). Although the bench studies showed that $\leq$ 60% impurities concentrations in recycled size formulations for ground yarns were acceptable in maintaining weave ability, a safety

margin was incorporated for ground yarns, designating the 45% impurities concentration limit in their recycled size formulations.

Griege cotton pile and ground yarns supplied for the scale-up trials by Frontier Spinning Mills were tested for cotton chemical impurities concentration achieved under the optimized, three-step desizing process (Section 4.3.2). Impurities extracted from both yarn constructions under the optimized desizing conditions constituted ~2.1% of the yarn masses. Yarn supplied by Frontier Spinning Mills was used for the thesis research work now onward and concluding the thesis.

The amount of virgin T-66 PVA to be added to the size formulation in each consecutive cycle of a recycling sequence to remain below the critical, maximum impurity concentration levels defined in the bench research were calculated for both pile and ground yarns. The calculated mass of virgin PVA to be added to each cycle's final size formulation for pile yarn was 20% of the original PVA mass used in the first slashing of the sequence, i.e., the conventional cycle, and for ground yarn, 40% (Figure 5.33, Appendix 2).

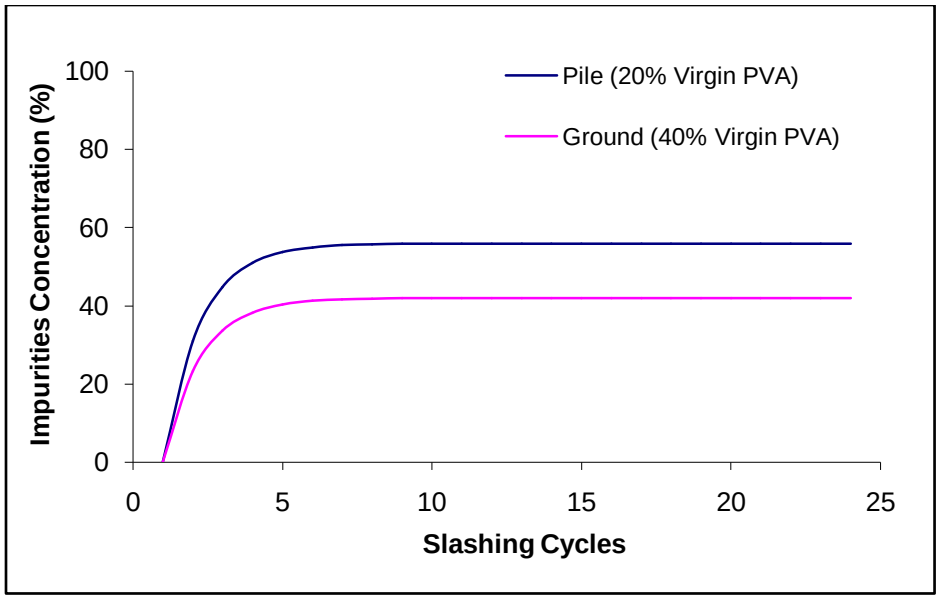


Figure 5.33: Calculated Impurities Concentration in T-66 PVA Size Formulations vs. Number of Slashing Cycles for Both Pile and Ground Yarns

Figure 5.33 clearly indicated that impurities concentration plateaus below the defined critical values could be achieved in six total slashing cycles with 20% and 40% virgin T-66 PVA adds to the recycled size formulation each reuse cycle for the pile and ground yarn, respectively. The Webtex® Pilot Slasher was utilized for the scale up slashing experiments (Section 4.2). Twelve warp ends were used in each slashing cycle. In consultation with WestPoint Home, solids size add-ons of 3% and 10% on yarn weight were decided for pile and ground yarns, respectively. Conventional residential towels manufactured by WestPoint Homes have ground, pile and filling yarns in a 1:6:1 mass ratio, respectively. Pile and ground yarns were slashed in the corresponding towel mass ratio.

The first slashing cycle was conducted as a conventional slashing (93% T-66 PVA/7% Seyco Superwax S size formulation), followed by five successive slashing cycles conducted utilizing the recovered PVA/cotton chemical impurities blended size

from the developed, three-step desizing/simulated VFE concentration process augmented by the proscribed, added virgin T-66 PVA (Section 4.3.4.2, Figure 5.33). Towel ground and pile yarns were slashed, whereas filling yarn was left as greige yarn.

When desizing constructed towels, filling yarn impurities are also extracted into the desize solution. Constructed towel desizing was simulated by mixing slashed ground, slashed pile and greige filling yarns in the same mass ratio as used in the WPH residential towel construction (1:6:1). Films were made from final pile and ground yarn recycled size formulations at every slashing cycle, and their tensile properties were tested. Similarly, slashed pile and ground yarn properties, e.g., tensile, abrasion resistance, hairiness, size penetration, yarn color and size add-on, were also tested.

5.6.1 Recycled T-66 PVA Size Formulation Film Tensile Properties

5.6.1.1 Breaking Strength

Film samples were prepared from the final recycled T-66 PVA size formulations and tested on the Instron Model 5567 Tester using ASTM Test Method D882-02. From Figure 5.34, the breaking strengths of the final recycled T-66 PVA formulation films for ground yarn increased after the first recycle (the second cycle size formulation) because wax was not added and the cotton chemical impurities had not built to a concentration sufficient to fully replace the effects of the 8% wax contained in the conventional size formulation, a fact beneficial to weaving efficiency. However, as predicted in the bench scale simulation studies, the recycled T-66 PVA size formulation film strength decreased in subsequent cycles, approaching a constant value plateau after the fourth slashing, as did the cotton chemical impurities concentration in the size. In the case of pile yarn, the recycled T-66 PVA size formulation film strength decreased with recycling because the

percentage of impurities in the first recycle size formulation was higher. With pile yarn, 20% based on original virgin T-66 PVA was added to the final size formulation each cycle, whereas with ground yarn, 40% was added. In the second slashing cycle with pile yarn, the impurities concentration in the final size formulation was close to that achieved in the fourth slashing cycle of the ground yarn, confirming the calculated levels (Figure 5.33). The breaking strengths of the recycled T-66 PVA size formulation films in the second and fourth slashing cycles of pile and ground yarn, respectively, were similar because of similar impurities concentrations in the size (Figure 5.33).

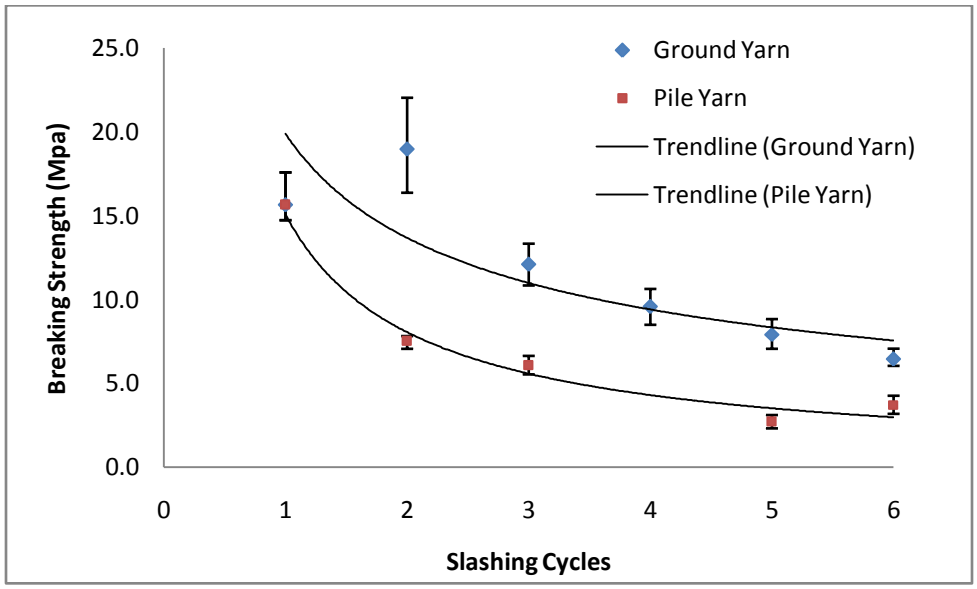


Figure 5.34: Changes in Breaking Strength of Recycled T-66 PVA Size Film vs. Slashing Cycles

5.6.1.2 Elongation at Break

With ground yarns, the elongations at break of recycled T-66 PVA size formulation films increased in the first size recycle, as most of the wax was replaced by

cotton chemical impurities and the impurities acted as a plasticizer in the corresponding film (Figure 5.35). Further increases in impurities decreased the films' elongations at break, approaching a plateau after 3-4 recycles. In the case of pile yarns, size film elongations at break behaved in a similar pattern to those for the ground yarns.

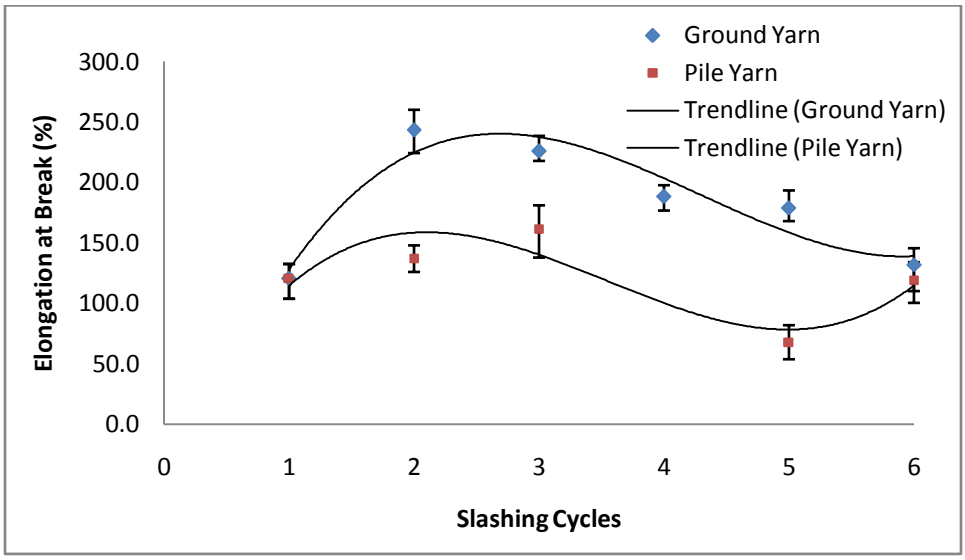


Figure 5.35: Changes in Elongation at Break of Recycled T-66 PVA Films vs. Slashing Cycles

5.6.2 Size Add-On

The size formulation mass concentrations were kept constant at 10% w/v for ground yarns and 3% w/v for pile yarns. Other slashing parameters, e.g., slashing speed, temperature and pressure were also kept constant. Although viscosities of the slashing formulations decreased with an increase in impurities (Section 5.3.3), size add-on showed consistency (10% of yarn weight for ground yarns, 3% for pile yarns, Figure 5.36). Linear density of the yarn, i.e., the yarn's tex, depended upon the size solids add-on. Because of the consistency in size add-on, recycled T-66 PVA slashed yarn linear density was nearly constant with the number of slashing cycles (Figure 5.37).

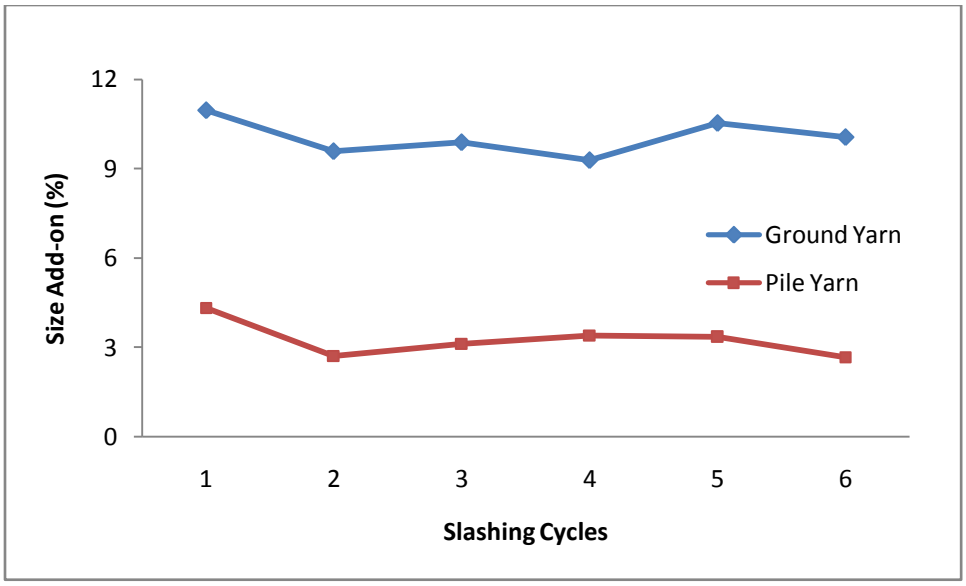


Figure 5.36: Size Solids Add-On of Recycled T-66 PVA Slashed Yarn vs. Slashing Cycles

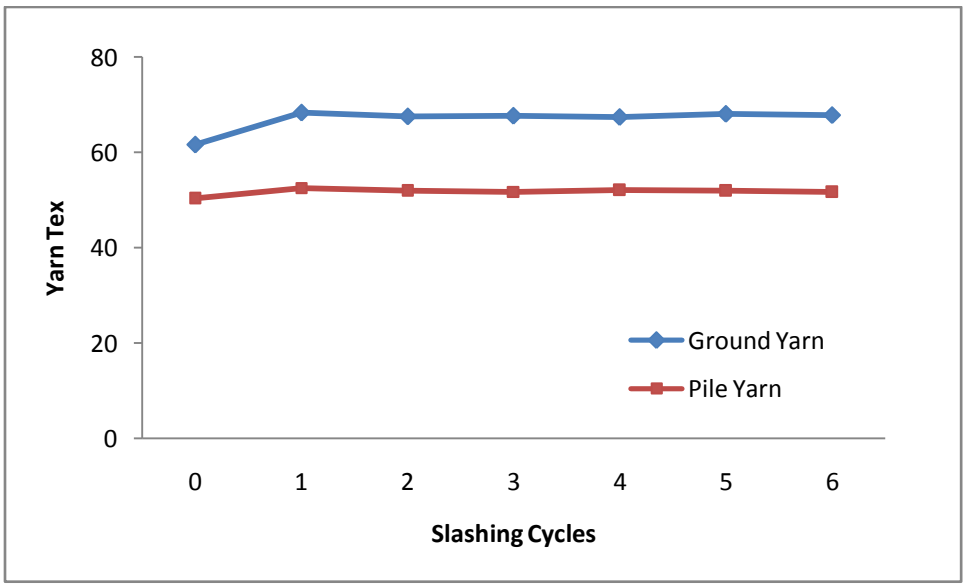


Figure 5.37: Yarn Tex of Recycled T-66 PVA Slashed Yarn vs. Slashing Cycles

5.6.3 Desized Efficiency of Recycled T-66 PVA Slashed Yarns

Desize efficiency of slashed yarn is important for further wet processing of the woven towel. Parallel to the WPH industrial desizing process, the developed three-step desizing method was used for the scale-up research trials (Section 4.3.4.2). Desize parameters such as temperature, time and liquor ratio were optimized so that 95% of the total size material was removed from the yarn. Using theoretical and experimental values (mass balance) of desize solids, desize efficiency was calculated. A desize efficiency close to 100% was achieved (Figure 5.38). The desize method was developed so that ≥95% of total size material can be removed. More than 100% desize efficiency indicated removal of >95% of total size material.

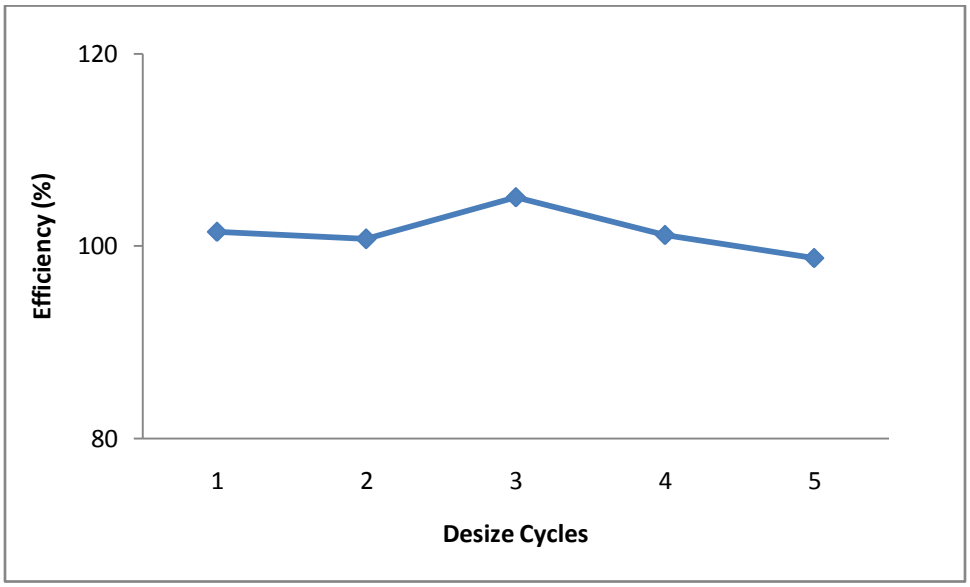


Figure 5.38: Desize Efficiency of Recycled T-66 PVA Slashed Yarn vs. Slashing Cycles

5.6.4 Influence of Low Molecular Weight Cotton Chemical Impurities on Viscosity Average Molecular Weight of Recycled T-66 PVA Size

Cotton chemical impurities extracted during the desize process were of low molecular weight, and their incorporation in the recycled size decreased the apparent average molecular weight of the material. Using dilute solution viscometry, the intrinsic viscosities of the pure T-66 PVA size and the recovered T-66 PVA/cotton chemical impurities blended size in the final formulation, i.e., after the proscribed virgin PVA add (20% of original), were measured for only the pile yarn in the second reuse cycle (Figures 5.39 and 5.40). The apparent intrinsic viscosity of the size dropped from 0.6 g/dL for the pure T-66 PVA to 0.4 g/dL for the size blend (recycled T-66 PVA/cotton chemical impurities/proscribed added virgin T-66 PVA) utilized for the third pile yarn slashing cycle of the reuse sequence. Considering the Mark-Houwink Equation, the values of constants K and α were assumed to be the same for both pure and recovered size.

$[\eta] = KM^{\alpha}$

K, α = constant

M = Viscosity-average molecular weight

A decrease in apparent intrinsic viscosity thus indicated a corresponding decrease in apparent viscosity average molecular weight of the size material.

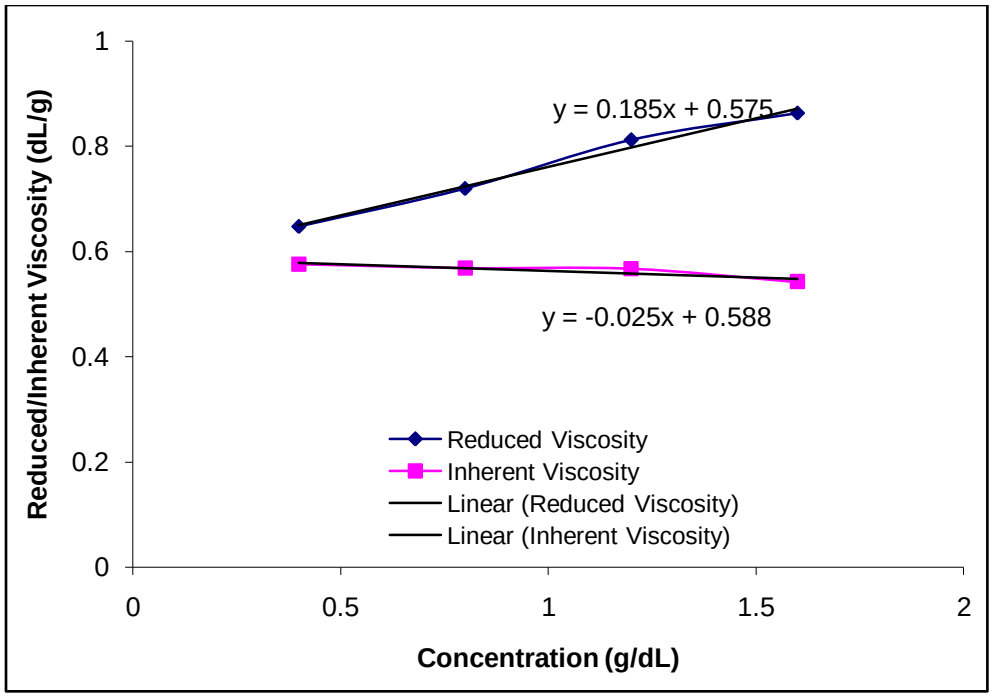


Figure 5.39: Viscosity vs. Concentration of Pure T-66 PVA Size in First Slashing Cycle (Conventional) Formulation

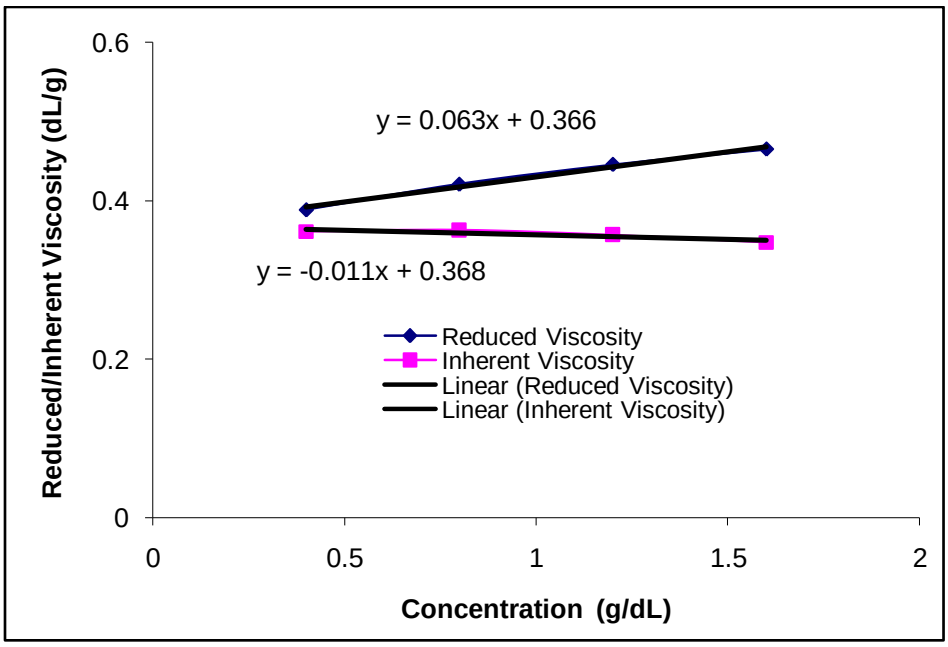


Figure 5.40: Viscosity vs. Concentration of Recycled T-66 PVA/Cotton Impurities Blended Size in Final Third Slashing Cycle Formulation

5.6.5 Change of Cotton Chemical Impurities Concentration in Size vs. Number of Slashing Cycles

Cotton chemical impurities concentration in the recycled size continued increasing each cycle early in a size reuse sequence, but after the fifth slashing cycle, they reached a plateau. The efficiency of desizing including removal of both T-66 PVA and cotton chemical impurities from the slashed yarns was calculated using mass balance, and the efficiency was determined to be close to 100%. The calculated and actual impurities concentrations in the recycled sizes were very close. Thermogravimetric Analysis (TGA) was used to measure the impurity percentage in the recycled size. Pure T-66 PVA, isolated cotton chemical impurities and the solids obtained by evaporating the water from the recycled blended size were separately incinerated at 650^{o}C using TGA (nitrogen gas flow) and their ash weights were measured (Figure 5.41). Using these data, the percentages of T-66 PVA and cotton chemical impurities in the desize solids were calculated. The cotton impurities and T-66 PVA theoretical and experimental values were very close (Figure 5.42, Appendix 1).

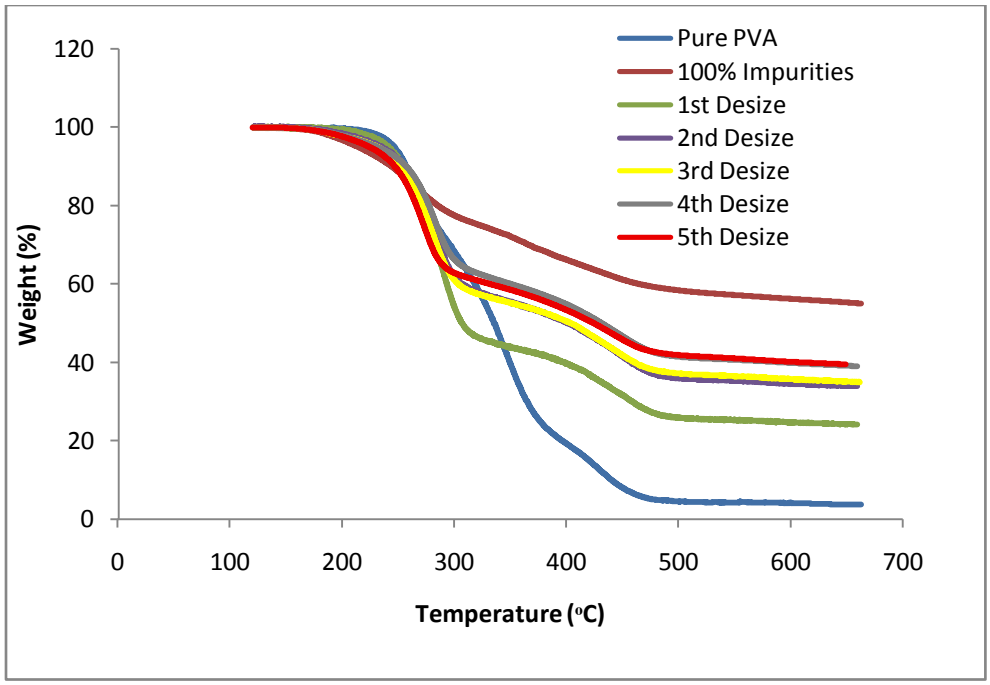


Figure 5.41: Changes in Weight Percentage of Desized Solids vs. Temperature

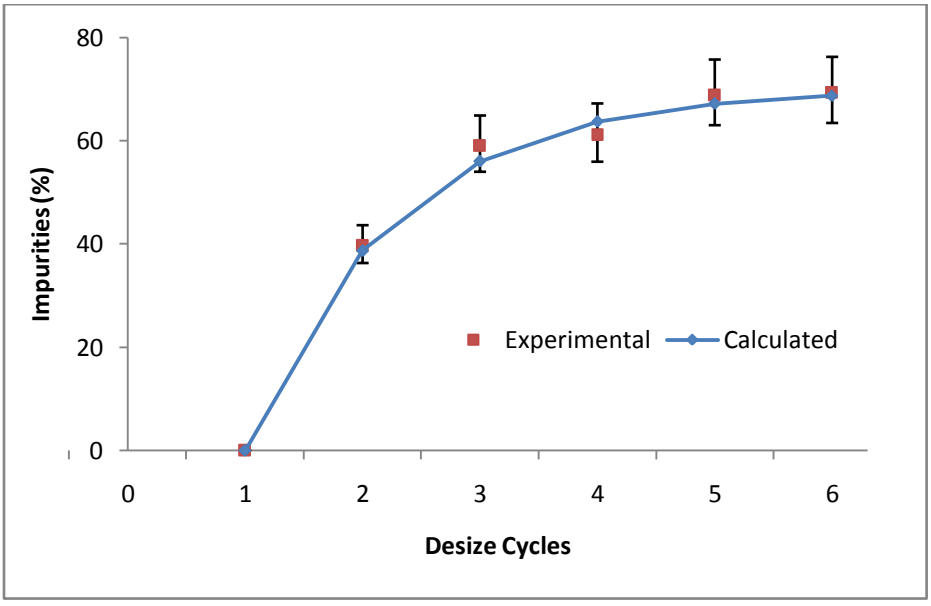


Figure 5.42: Percentage Cotton Impurities in Recycled T-66 PVA Size vs. Slashing Cycles

5.6.6 Size Penetration

The efficiency of size diffusion inside the slashed yarn was visually observed by adding tracer dye (C. I. Basic Violet 10) to the size formulation. Samples of slashed pile yarn (3% of yarn weight solids add-on) cross sections were made and viewed under the Leica Microscope (Section 4.3.10.6). The micrographs indicated that the bulk of the size was concentrated on the surface of the yarn in the initial cycles of a slashing sequence, but with an increase in the number of slashing cycles, the size penetrated deeply inside the yarn core. In the fifth slashing cycle, the size actually penetrated to the core of the yarn (Figures 5.43-5.48). A similar trend was seen with the ground yarn (10% of yarn weight solids add-on, Figures 5.49-5.54). As the low molecular weight cotton chemical impurities increased in concentration in the final size formulations, apparent viscosity decreased, facilitating size penetration into the yarn diameter.

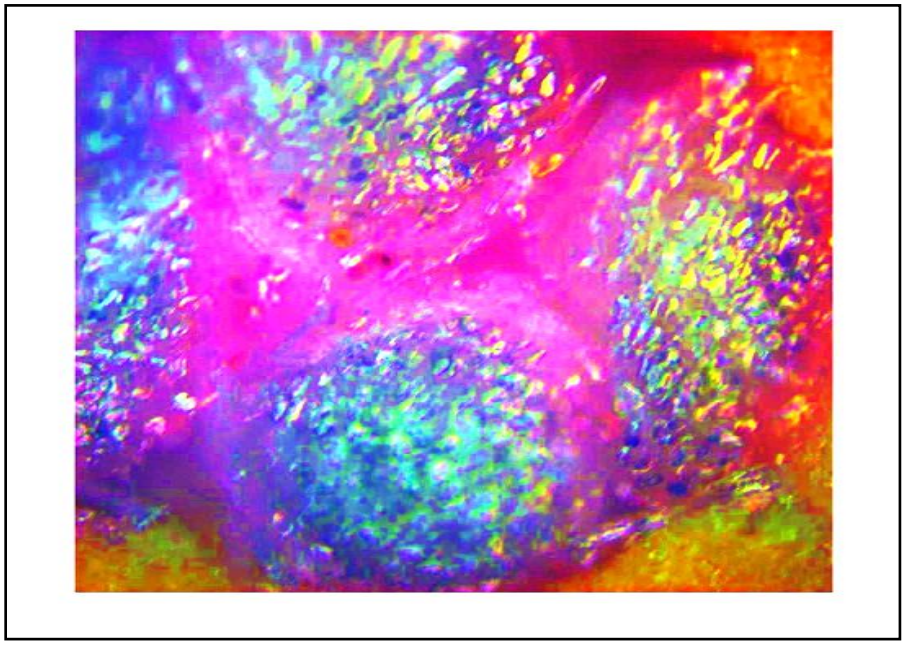


Figure 5.43: Size Penetration in Pure T-66 PVA Slashed Pile Yarn

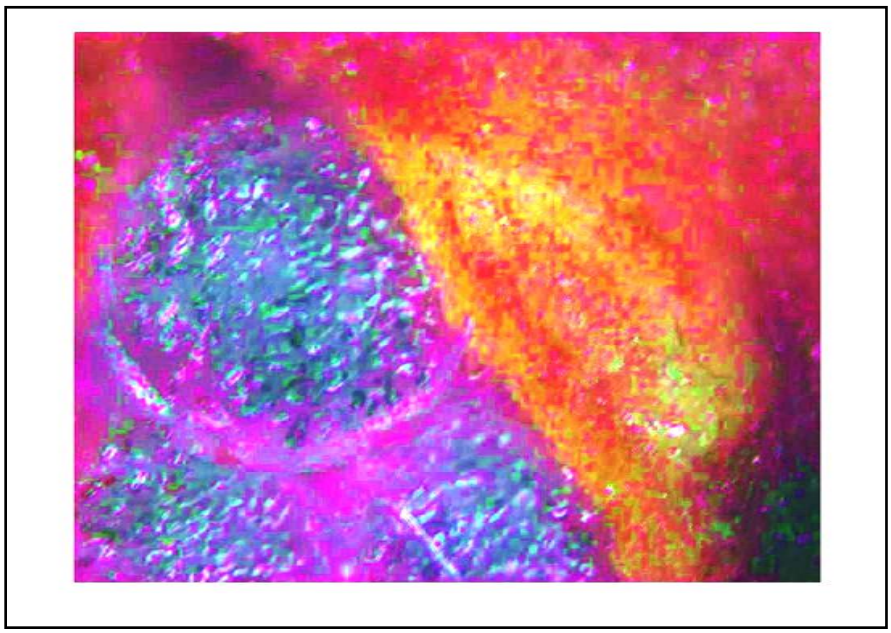


Figure 5.44: Size Penetration in First Recycle T-66 PVA Slashed Pile Yarn

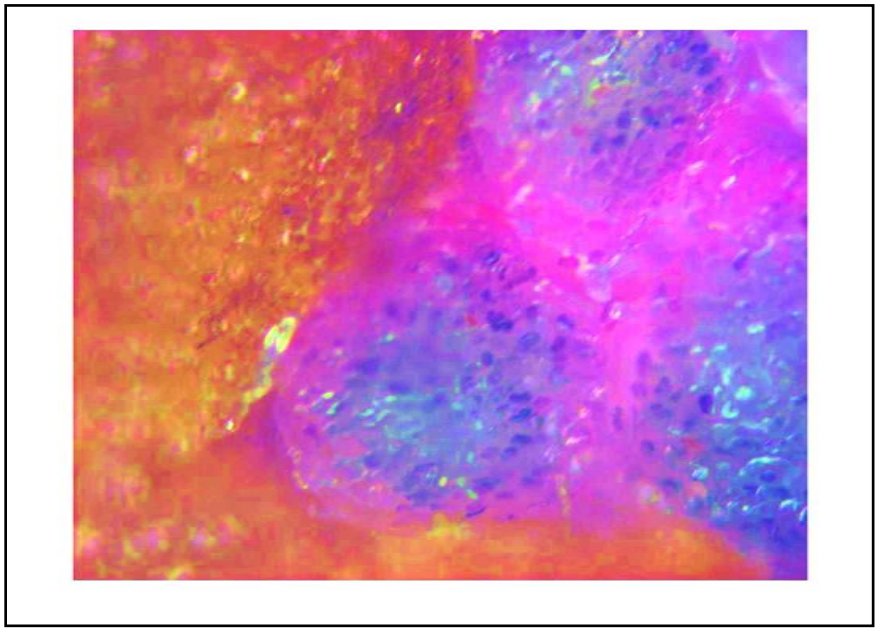


Figure 5.45: Size Penetration in Second Recycle T-66 PVA Size Slashed Pile Yarn

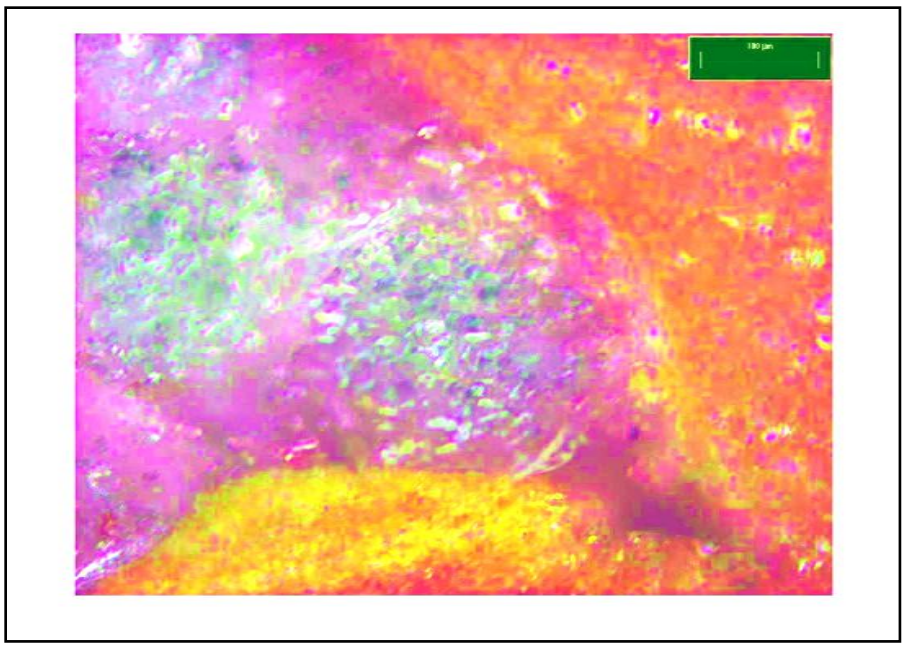


Figure 5.46: Size Penetration in Third Recycle T-66 PVA Slashed Pile Yarn

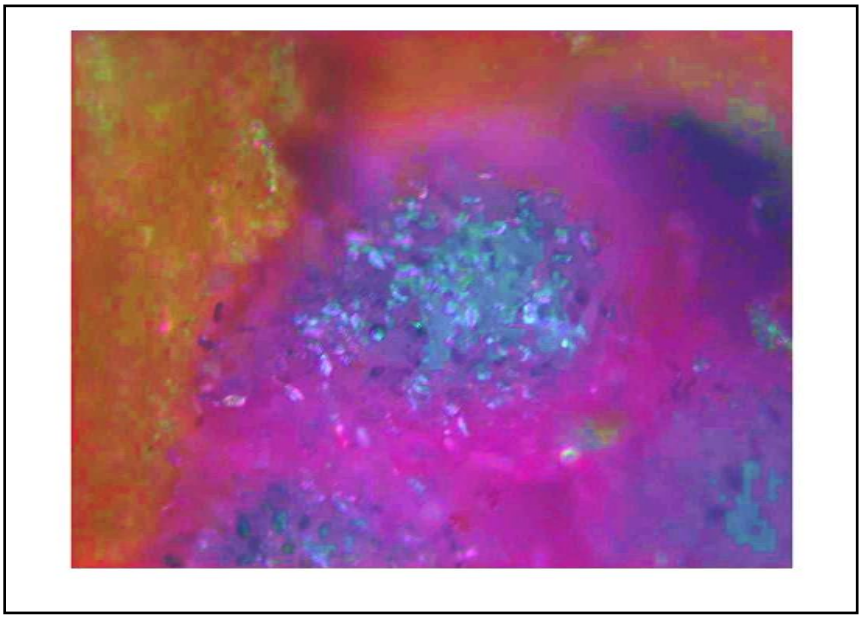


Figure 5.47: Size Penetration in Fourth Recycle T-66 PVA Slashed Pile Yarn

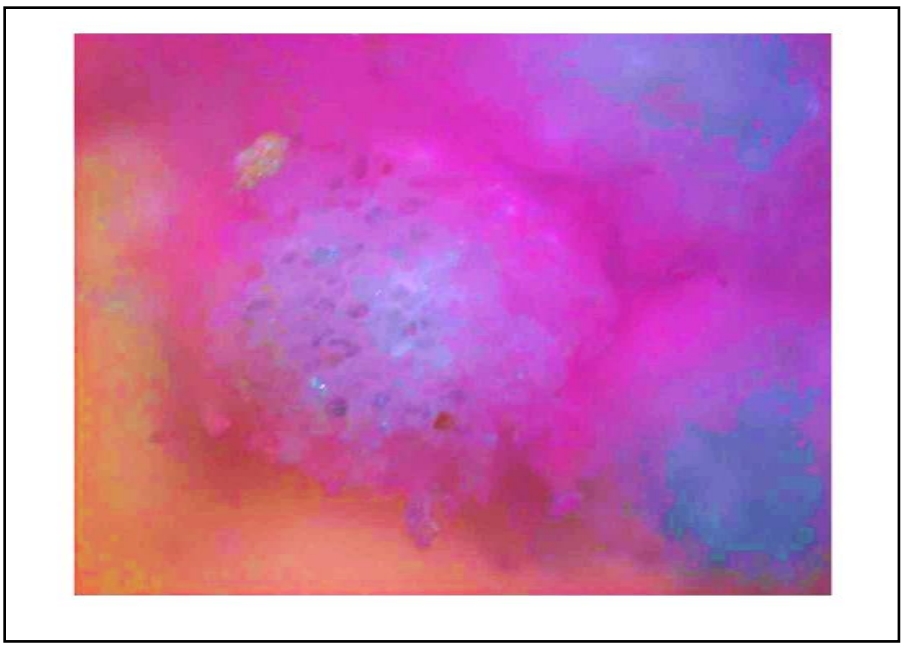


Figure 5.48: Size Penetration in Fifth Recycle T-66 PVA Slashed Pile Yarn

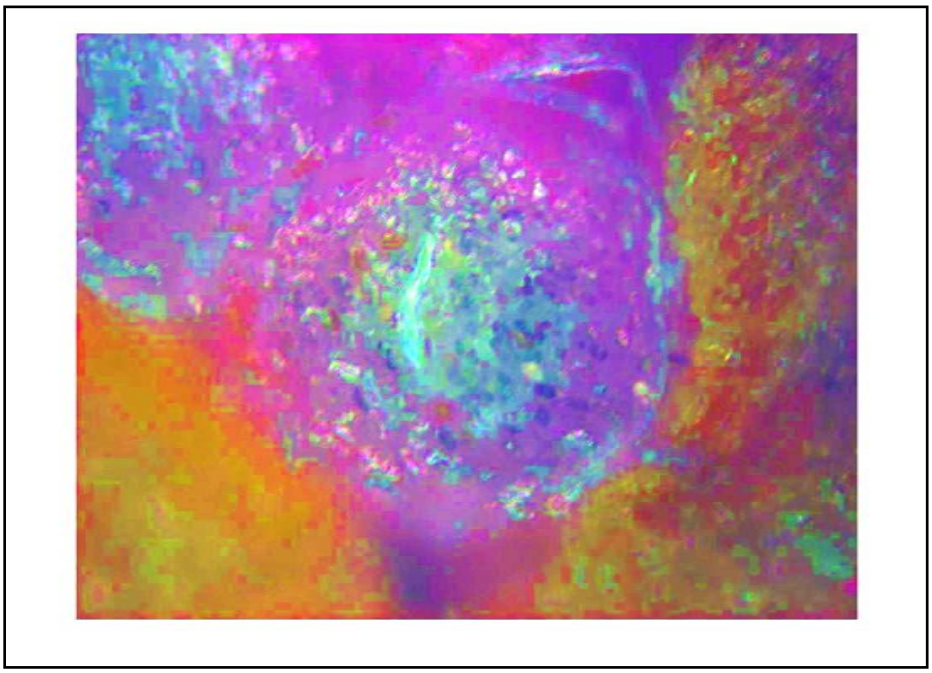


Figure 5.49: Size Penetration in Pure T-66 PVA Slashed Ground Yarn

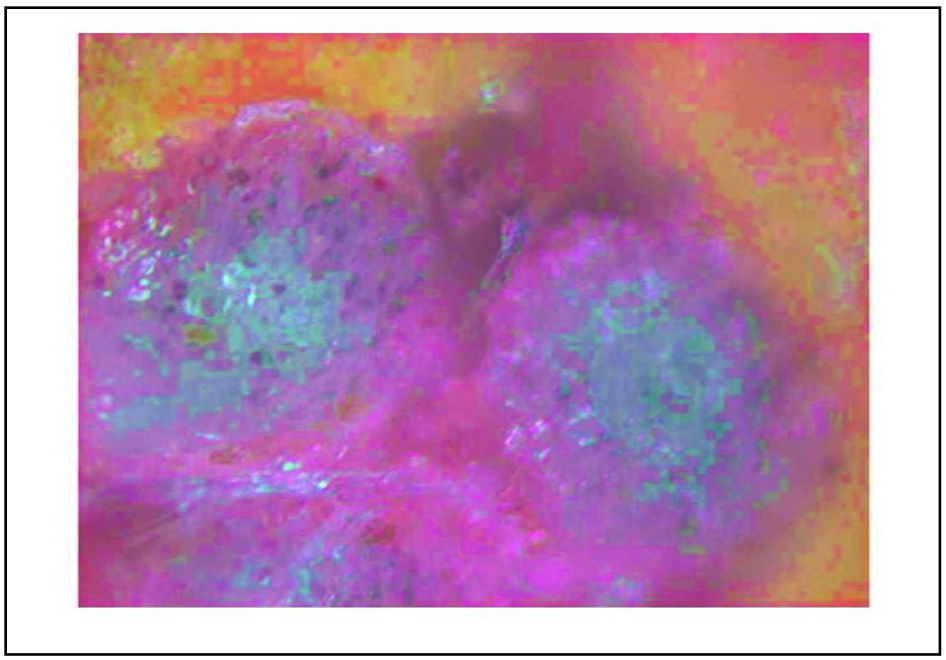


Figure 5.50: Size Penetration in First Recycle T-66 PVA Slashed Ground Yarn

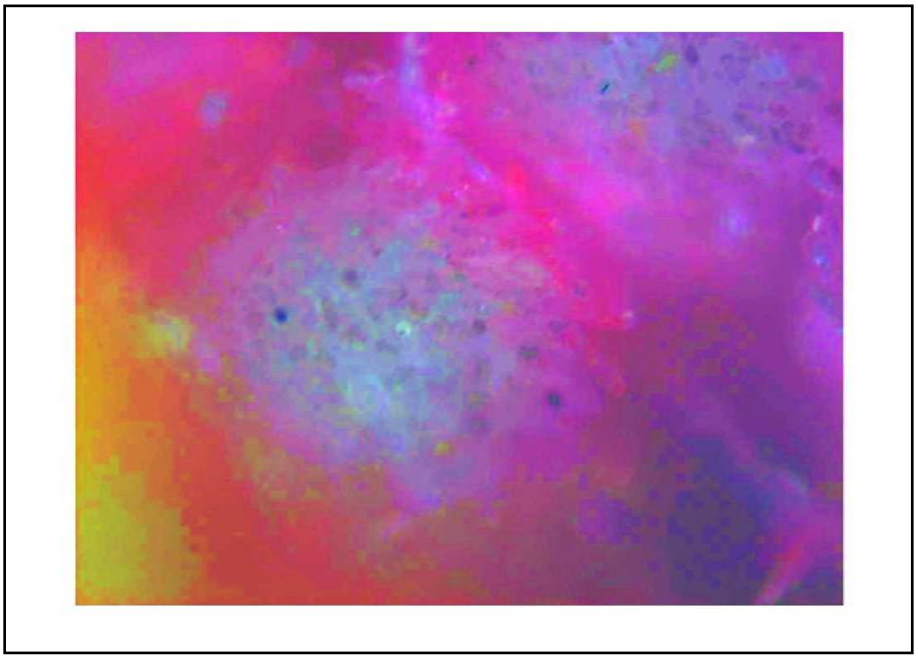


Figure 5.51: Size Penetration in Second Recycle T-66 PVA Slashed Ground Yarn

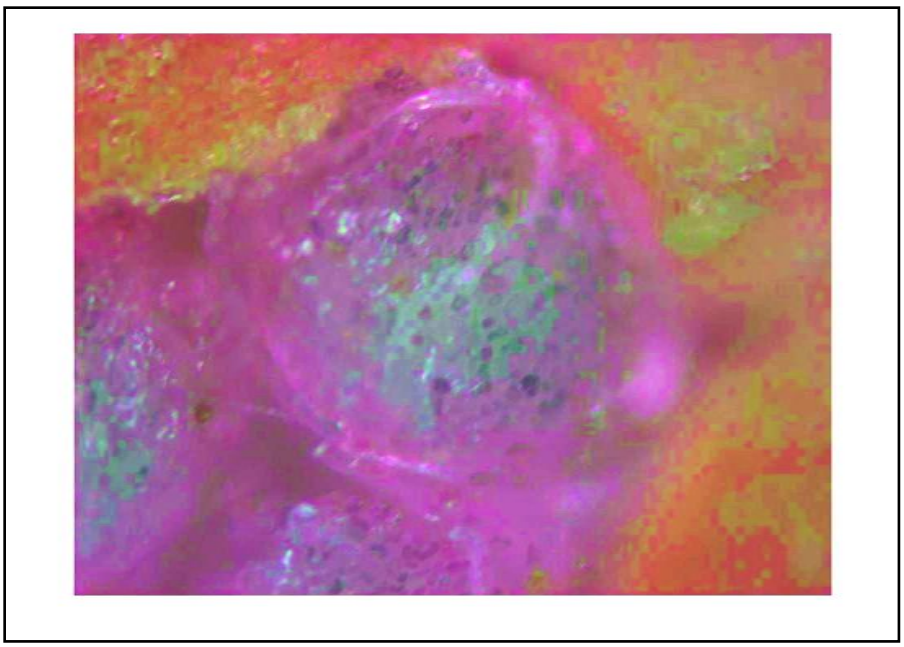


Figure 5.52: Size Penetration in Third Recycle T-66 PVA Slashed Ground Yarn

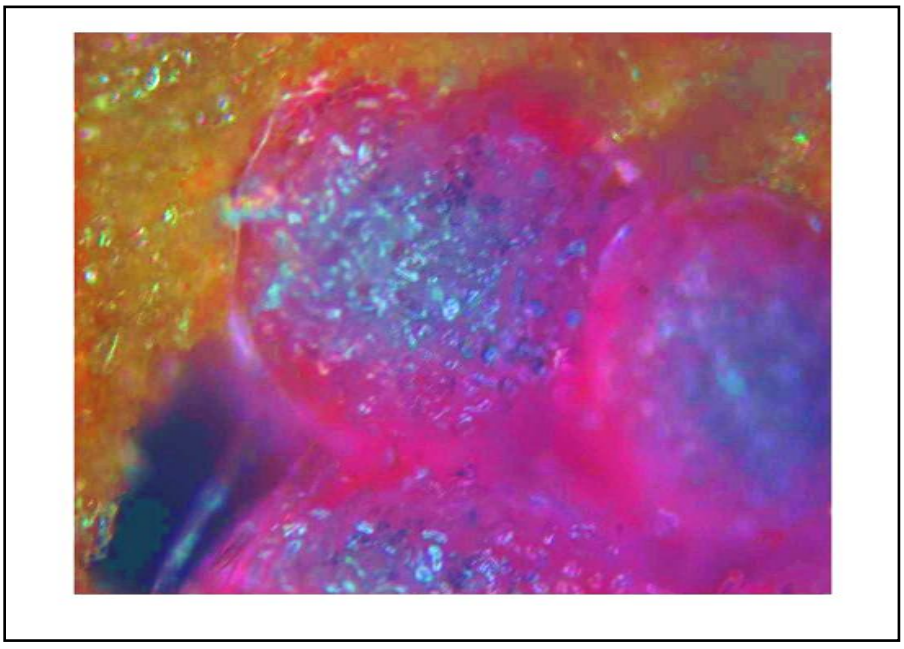


Figure 5.53: Size Penetration in Fourth Recycle T-66 PVA Slashed Ground Yarn

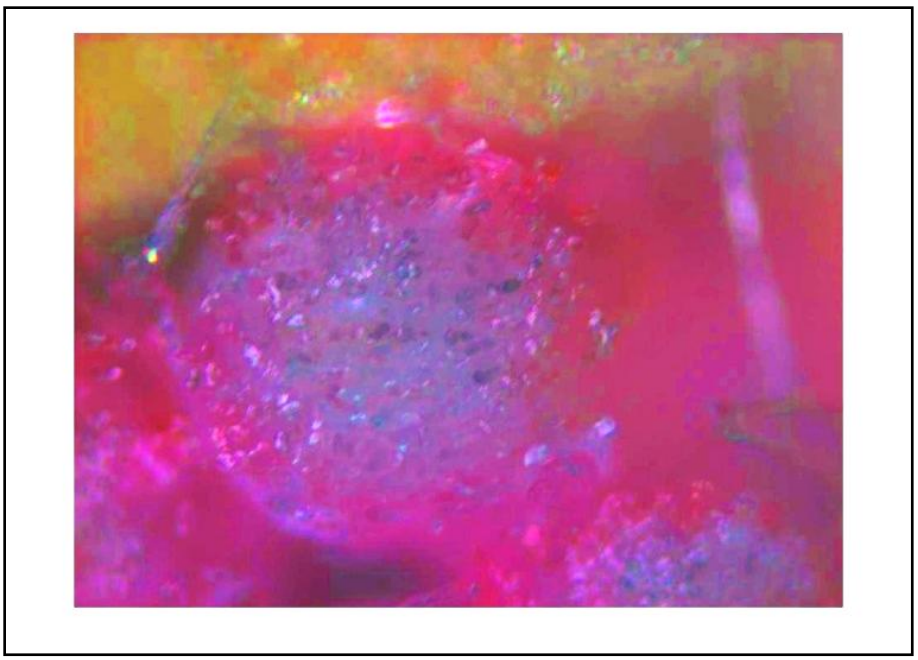


Figure 5.54: Size Penetration in Fifth Recycle T-66 PVA Slashed Ground Yarn

5.6.7 Slashed Yarn Tensile Properties

5.6.7.1 Load at Break and Tenacity

As expected, recycled T-66 PVA slashed yarn showed an increase in load at break. In Figure 5.55, loads at break for both pile and ground yarns increased more than 20% over that of greige yarn, and as a result, tenacities of the slashed yarns also increased (Figure 5.56). Load at break initially increased as wax was replaced by impurities, but on further increase in impurities concentration in the size, load at break and tenacity decreased. After the first size reuse cycles for both yarns, the slashed yarn loads at break and tenacities were nearly constant for subsequent slashings.

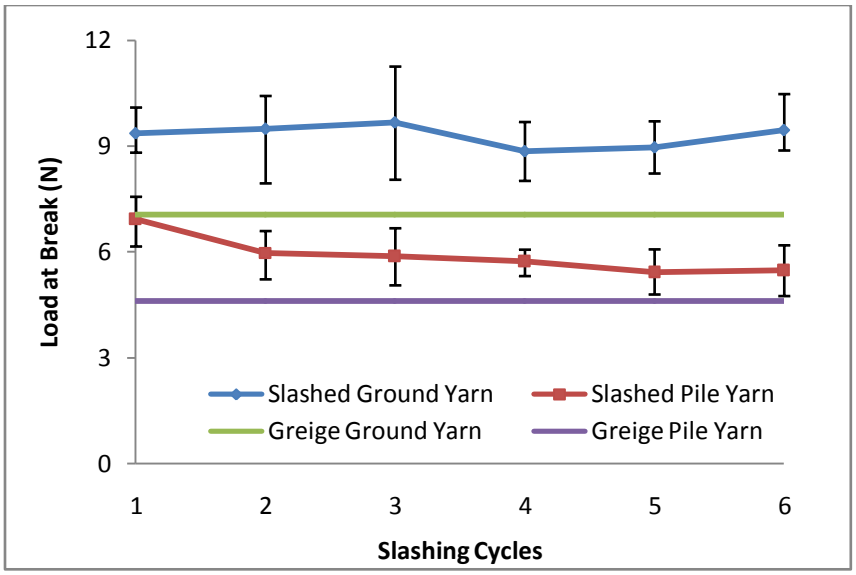


Figure 5.55: Load at Break of Recycled T-66 PVA Slashed Yarn vs. Slashing Cycles

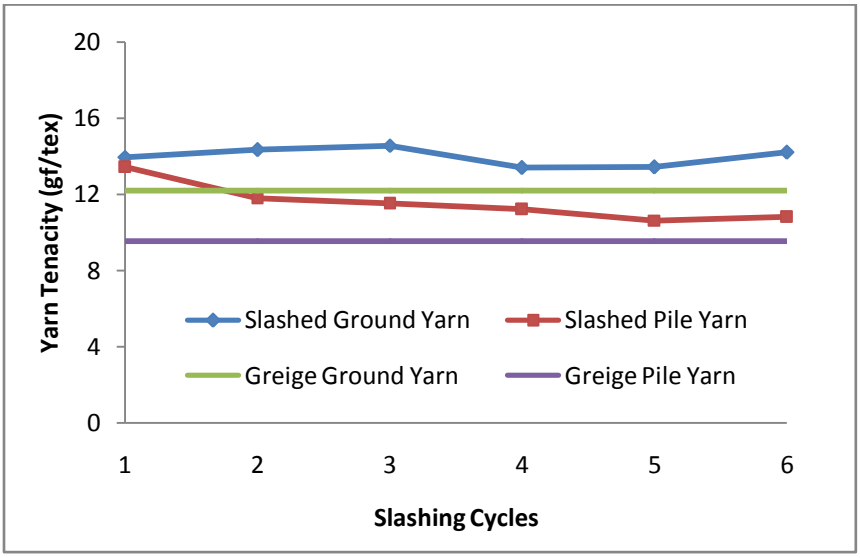


Figure 5.56: Tenacity at Break of Recycled T-66 PVA Slashed Yarn vs. Slashing Cycles

5.6.7.2 Yarn Elongation at Break

The elongation at break of slashed yarn was expected to decrease compared to that of greige yarn, as fibers in the slashed yarn stick to each other and prohibit both

elongation of individual fibers and fiber slippages. In the case of slashing with recycled T-66 PVA size, yarn elongation at break increased because of low molecular weight cotton chemical impurities occluded in the recycled size. The low molecular weight impurities, apart from lubricating fibers to facilitate slippage, acted as plasticizers in the recycled T-66 PVA size films, increasing their elongations at break (Section 5.6.2.2). Figure 5.57 shows that elongation at break of slashed ground yarns (10% solids add-on) decreased after the third slashing cycle because of the increased impurities concentration in the recycled size. Pile yarns (3% solids add-on) showed a decrease in elongation at break after the first (conventional) slashing because of the high percentage of impurities in the first recycled size formulation. In both yarn cases, the elongation at break of recycled T-66 PVA slashed yarn was closer to the proscribed industrial limit (decrease not less than 20% of the elongation to break of the corresponding greige yarns).

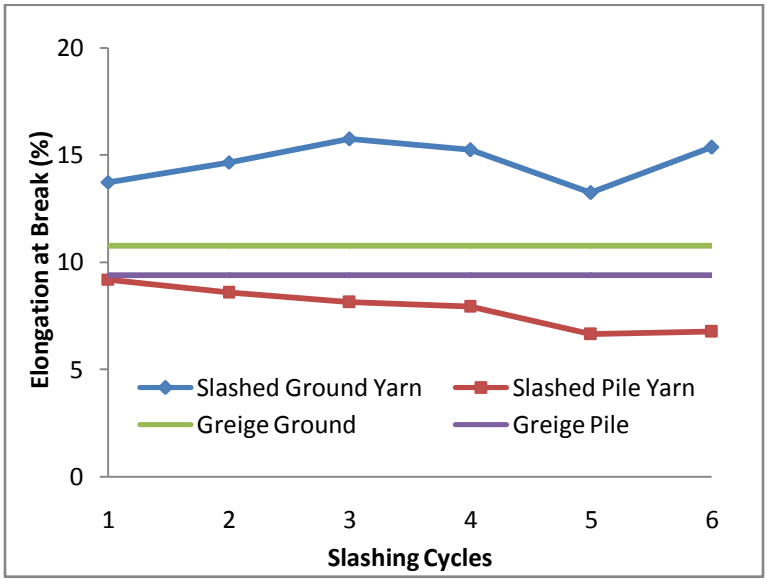


Figure 5.57: Elongation at Break of Recycled T-66 PVA Slashed Yarn vs. Slashing Cycles

5.6.8 Work of Rupture of Recycled T-66 PVA Slashed Yarns

In Figure 5.58, the work of rupture of recycled T-66 PVA slashed ground yarns initially increased with cotton chemical impurities concentration, but decreased after the third slashing cycle. The work of rupture decreased because the higher concentrations of impurities in later size reuse sequence cycles decreased both the breaking load and the breaking elongation of the yarn. Similar behavior was observed with the pile yarn. Both ground and pile yarn works of rupture were more than or near the proscribed limit for the slashed yarns (~those of the corresponding greige yarns).

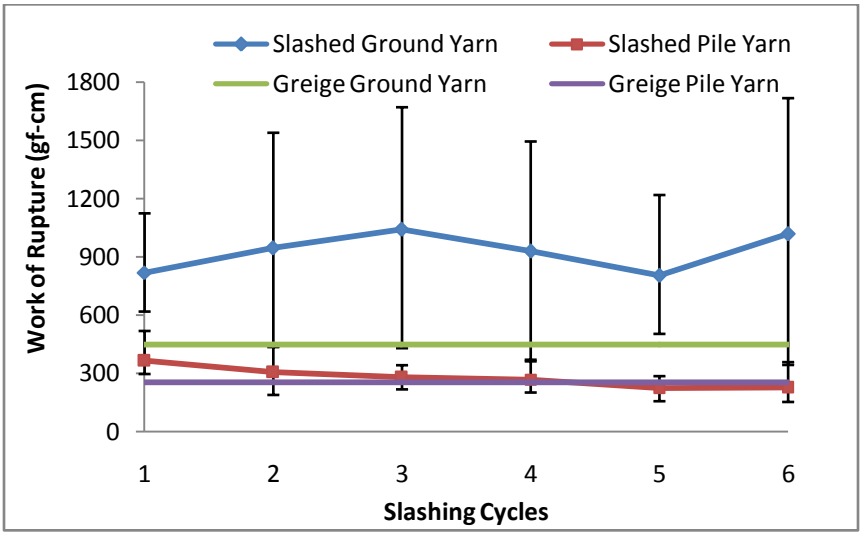


Figure 5.58: Work of Rupture of Recycled T-66 PVA Slashed Yarn vs. Slashing Cycles

5.6.9 Bending Length

Slashed yarn stiffness was measured by its bend in length under its own weight at a constant angle (41.5^{o}). With slashed ground yarn, the bending length initially decreased with increasing cotton chemical impurities concentration in the recycled size, but after

the third slashing cycle (second size reuse), the bending length remained nearly constant (Figure 5.59). A similar trend was observed with slashed pile yarns.

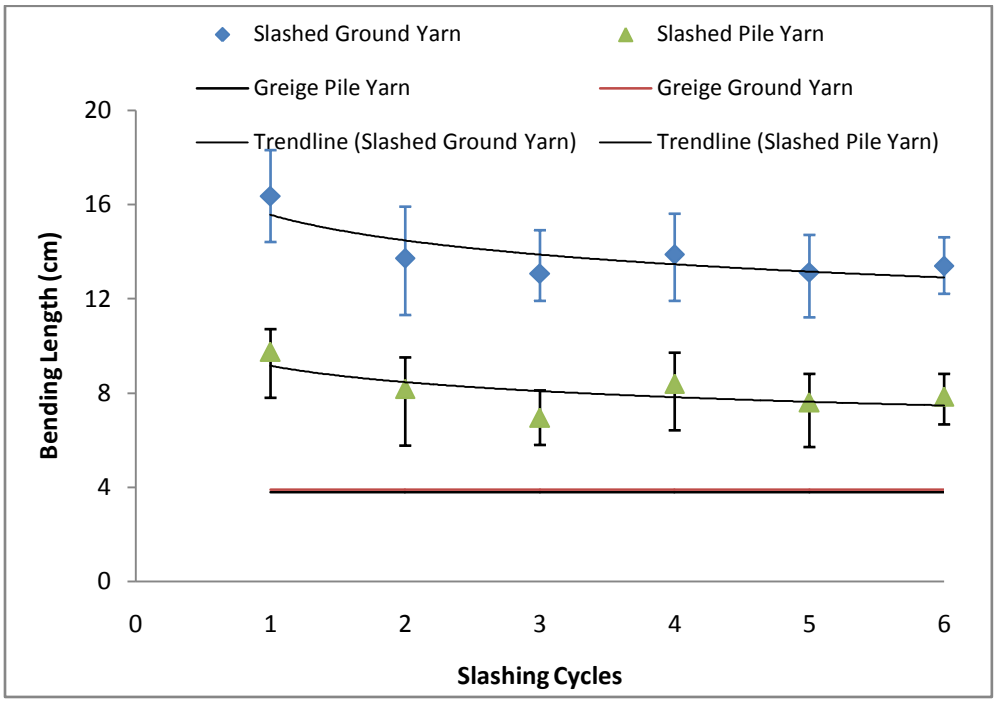


Figure 5.59: Bending Length of Recycled T-66 PVA Slashed Yarn vs. Slashing Cycles

The towel manufacturing industry currently uses a PVA/starch blended size (60/40) for slashing towel pile yarns, as pure PVA /wax slashed yarn is stiff, inhibiting the ability of the terry weaving machine to loop it (Appendix 3) [28]. The reported favorable yarn stiffness results will encourage the use of VFE recycled PVA for slashing pile yarns entering woven terry towel constructions.

5.6.10 Yarn Hairiness

Samples were prepared and the hairs were measured using the Tray Fray Counter. In Figure 5.60, recycled T-66 PVA slashed yarn hairiness was nearly constant in both the pile and ground constructions. Compared to the corresponding greige yarn, the slashed ground yarn hairiness (2 mm hair length) dropped approximately 90% because of the high percentage (10% of yarn weight) of size add-on, whereas slashed pile yarn hairiness dropped approximately 50% compared to the greige yarn because of the lower size add-on (3% of yarn weight).

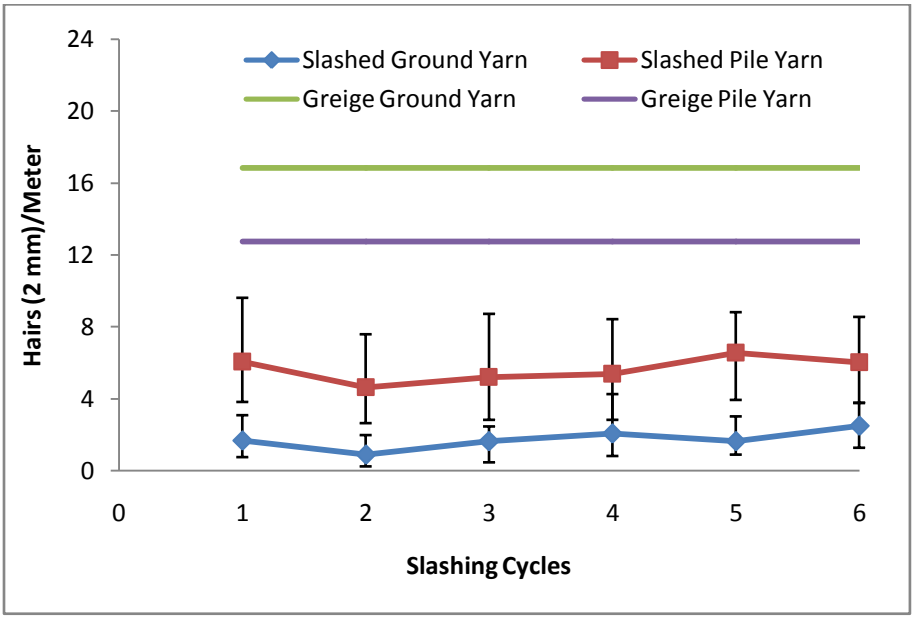


Figure 5.60: Recycled T-66 PVA Slashed Yarn Hairiness vs. Slashing Cycles

5.6.11 Abrasion Resistance

Abrasion resistance is an important property of slashed towel ground yarns, and to a lesser extent pile yarns, as abrasion against metal parts of modern high-speed weaving

machines is a major factor in warp yarn breaks. The number of abrasion cycles to first yarn break as determined on the Ruti Webtester is an indirect measurement of the weave ability of slashed warp yarns (Section 4.3.10.3). Fifteen yarn samples (either slashed ground or pile yarns) were mounted and the number of abrasion cycles achieved against the vertical round/square metal rods of the instrument to first yarn break was recorded. The average of four such tests was then calculated for each slashed yarn type (Figure 5.61). After the first (conventional) slashing cycle, the number of abrasion cycles to first yarn break achieved with the ground construction increased, but after the second slashing (first size reuse) cycle, it remained nearly constant. The 8% wax in the initial (conventional) T-66 PVA size formulation reduced the yarn surface friction, which aided in increasing the number of abrasion cycles to first yarn break beyond that of the greige yarn. At the same time, an increase in cotton chemical impurities concentration in the recycled size reduced the film thickness on the yarn. Ground yarns slashed in subsequent size reuse cycles maintained similar abrasion resistance, as the increased concentration of cotton impurities mimicked the wax's lubricity and PVA film plasticization performances in the first slashing cycle. A similar trend was initially seen for the slashed pile yarns, but after the third slashing (second size reuse) cycle, the number of abrasion cycles to first yarn break decreased slightly with recycle number because of the low size solids add- on (3% of yarn weight vs. 10% for the ground yarn) and the increasing impurities concentration in the recycled size films.

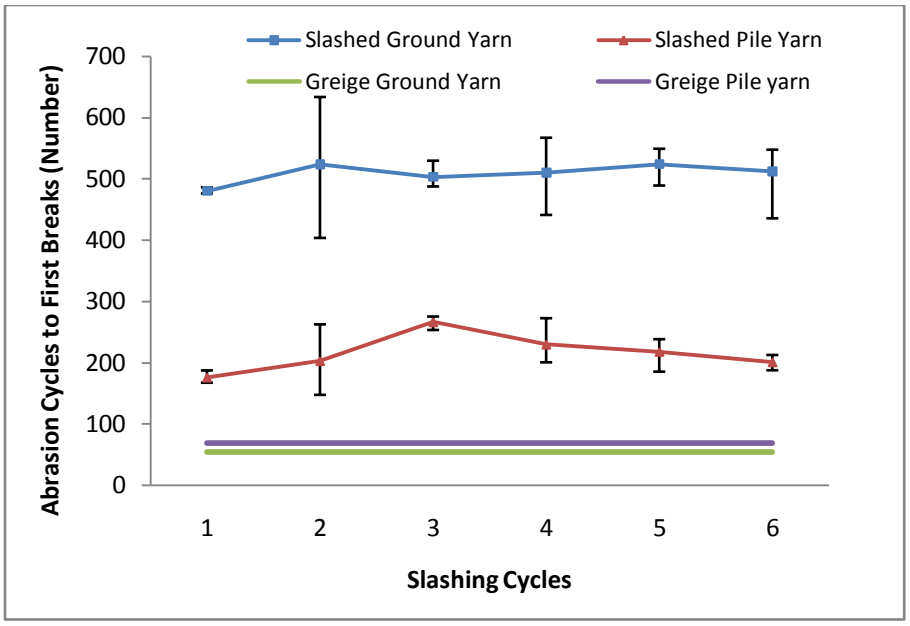


Figure 5.61: Abrasion Cycles to First Yarn Break of Recycled T-66 PVA Slashed Yarn vs. Slashing Cycles

5.6.12 Desized Yarn Color

The color of the recycled size formulations turned yellow then light brown in slashing sequences because of increases in cotton impurities concentrations as well as chromophore formation due to PVA degradation on the steam cans, similar to what has been reported in UF PVA size concentration/recycling processes [28, 29]. The light brown color of the recycled size formulation caused the slashed yarns to appear slightly darker than both the greige yarns and the first cycle (conventional) slashed yarns. For dyeing light pastel shades, all of the colored impurities should be removed during desizing. Samples were made by randomly wrapping under slight tension both desized ground and pile yarns close to each other on piece of rectangle cardboard previously covered with a piece of white photocopy paper to give a relatively smooth, fabric-like surface. Desized yarn CIE color values ΔL, Δa and Δb were measured on the MiniScan

Reflectometer using the white tile as the standard, whereas the overall color difference, ΔE, was calculated using the first cycle (conventional) slashed desized yarn as the standard (Section 4.3.13). The desized yarns' ΔL, Δa and Δb values were similar, the calculated ΔE was approximately one (Figure 5.62-5.63).

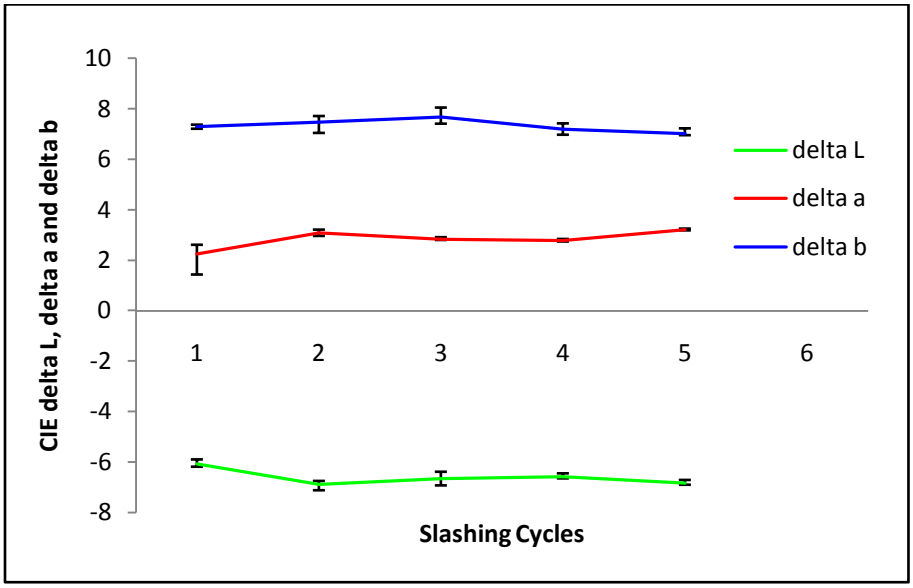


Figure 5.62: Desized Yarn CIE ΔL, Δa and Δb Values vs. Slashing Cycles

Figure 5.63: Desized Yarn CIE ΔE Values vs. Slashing Cycles

5.7 Economic Viability of VFE Incorporation

Economic studies were first conducted at a model towel plant scale (~100,000 gal/day of desize effluent stream treated) on recovery and recycling of T-66 PVA size using VFE as the concentrating technology. The results were compared with those calculated for the conventional PVA/starch (60:40) blend slashing process without size recovery and with POTW treatment of the desize effluent (Appendix 5). For calculating the operating costs of the model plant-scale VFE unit, energy, labor and maintenance costs were considered. To calculate the benefits from VFE incorporation, savings from reduced water consumption, reduced energy to heat water, T-66 PVA recycling, wax deletion in recycled size formulations and reduced waste water treatment costs were considered. The overall VFE economic study was conducted in consultation with the partner manufacturer, VACOM, LLC, coupled with data available from the literature [1,

5, 63, 72]. Assumptions made in the study was, no loss of water or size mass occurred in the handling/transportation of the materials, e.g., pipe losses.

A commercial-size model towel manufacturing plant was considered whose capacity was 143,700 lb of product/day. The model plant produced ~100,000 gallons of 1% w/w solids desize effluent stream/day when all-PVA/wax was used as the size in slashing irrespective of what size concentration technology was incorporated, whereas it produced ~175,000 gallons of 1% w/w solids desize effluent stream/day when a conventional PVA/starch (60:40) blended size was used in slashing with no size recycle. Conventional slashing in the model plant produced more desize liquor because of the higher size solid add-ons utilized than for the PVA/wax size (7% solids add-on for pile yarn and 20% for ground yarn in the conventional PVA/starch process, 3% for pile and 10% for ground yarns in the PVA/wax process) [28, 36]. For the model towel manufacturing plant, incorporation of the VFE technology for PVA recovery and recycling resulted in ~$3.2M a year in savings compared to the current PVA/starch process with no size recycling (Appendix 5).

Surprisingly, the effect of a rise in energy prices had little impact on the cost savings. In this study, the current energy price of natural gas (the normal energy supply for plant boilers) was $10/MBtu. If the price suddenly doubled as it did in July, 2008, i.e., to $20/MBtu, than in the case of VFE incorporation into the model plant the total operational cost savings over the conventional size blend process with no recovery would increase to only ~$3.4M/year, with the increase in savings of $0.2 M/year due to the recovered hot water stream emanating from the condensed steam. The VACOM, LLC VFE unit recovers up to 90% of the total energy input to the process [1]. The energy

required to operate the VFE unit is less than the energy required to heat water from 16^{o}C to 90^{o}C.

The raw return on capital investment (R0I) period for VFE incorporation in the model plant was less than one year, based on an ~$3M total capital investment cost for the model plant provided by VACOM, LLC. VFE unit manufacturers also claim that if the recovered material has some inherent value, then the raw ROI of installing a plant-size unit for material concentration and recovery could be as little as a few months to a year [20].

CHAPTER 6

CONCLUSIONS

Based on the results obtained from the bench research on the properties/utilization of recovered T-66 PVA size films and subsequent slashed yarns, no added wax was required in the final recycled size formulations, as the cotton chemical impurities extracted into the desize effluents performed the same functions on the slashed yarns as the wax. The maximum cotton chemical impurities concentration levels in the recycled size for viable towel weaving were determined to be 60% for the pile yarn and 45% for the ground yarn, respectively. Correspondingly, the optimum adds of virgin T-66 PVA to the final recycled size formulations were determined to be 20% of original mass for pile yarn slashing, and 40% of original mass for ground yarn slashing, respectively. The optimized results from the bench scale research were successfully used to conduct proof of concept, scale-up slashing trials with both pile and ground towel yarns on a continuous Webtex® Pilot (12 end warp) Slasher.

Conclusions from the bench scale research were:

- In VFE, the recycled T-66 PVA desize effluent stream entrained extracted cotton yarn chemical impurities (~2.3% of yarn weight per desize cycle, Springs Industries 100% cotton constructions). The apparent MW average of the recycled T-66 PVA size decreased accordingly, as the impurities were of lower molecular weight than the polymeric T-66 PVA.
- The breaking strength of the recycled T-66 PVA size film initially decreased with increasing impurities concentration in the size, and reached

a plateau at ≥25% impurities concentration. The addition of wax to pure T-66 PVA size decreased the film strength in a similar manner. With the occluded cotton impurities performing the same functions on the slashed yarn as wax, no wax adds to the final recycled T-66 PVA size formulations were required.

- Elongations at break of recycled T-66 PVA size films initially increased with impurities concentrations in the size, but at ≥35% concentration, the elongation to break decreased. In a like manner, the pure T-66 PVA size films' elongations to break also decreased with increasing wax percentages. An increase in elongation at break of recycled T-66 PVA film leads to more efficient weaving processes compared to the pure polymer film [73].
- The modulus of elasticity of recycled T-66 PVA size film decreased with increasing cotton chemical impurities concentration, facilitating terry towel weaving.
- The contact angle of water droplet (wet ability) on recycled T-66 PVA size film decreased with increasing impurities concentration. The VFE recycled T-66 PVA size film is thus easy to wet, facilitating effective desizing of the fabric.
- The viscosities of the final recycled T-66 PVA size formulations decreased with increasing impurities concentrations, aiding in uniform size pick-up in slashing at low temperatures.

- The bust rod resistance forces of the bridged films of the recycled T-66 PVA slashed yarns initially increased with increases in impurities concentrations, but at $\geq$25% impurities concentration in the size, they decreased, reaching zero at 100% impurities level (no PVA in the size). A similar trend was observed with increasing wax percentages in pure T-66 PVA films. In slashing, since most of the yarn breaks and generation of hairiness occur at the bust rods, any decrease in bust rod resistance will decrease both.
- Although at constant total solids concentration the viscosities of the recycled size formulations decreased, the resulting slashed yarns exhibited constant size solids add-ons. This trait should lead to more facile control of the slashing process (Section 5.3.3).
- Slashed yarn load at break initially increased with recycling number, but after the third recycle, it decreased slightly and then remained constant. The slashed yarn loads at break for all the processed materials were at or near acceptable levels, i.e., 20% greater than those of the corresponding greige yarns (Section 5.4.2.1).
- The slashed ground yarn elongations at break initially increased with size recycling number and remained constant on further slashing cycles. The slashed pile yarn elongation at break decreased with size recycling number, but it was greater or near to the acceptable limit in all cases, e.g., $\geq$80% of that of the greige yarn.

- Slashed ground and pile yarn works of rupture initially increased and then decreased with size recycling number, but they were more than or close to the acceptable limit, e.g., approximately equal to that of the corresponding greige yarns.
- Ground yarn hairiness decreased after slashing, but remained constant throughout the size recovery/recycling sequences. This characteristic will lead to fewer warp yarn breaks in air jet weaving.
- Abrasion cycles to first slashed ground yarn breaks increased after slashing compared to the greige yarns, but remained constant throughout the size recovery/recycling sequences. This trait will reduce warp yarn breaks in weaving, improving efficiencies.

The conclusions from the proof of concept scale-up slashing trials utilizing recycled T-66 PVA size formulations were:

- The scale up trials confirmed the recycled T-66PVA film and slashed yarn results, i.e., the recycled size film breaking strengths and elongations at break, coupled with slashed yarn loads at break, tenacities, elongations at break, works of rupture, abrasion cycles to first yarn breaks, hairiness and bust rod resistances, were all maintained throughout the six cycle slashing sequences at levels sufficient for effective towel weave ability.
- The scale up trials verified that 20% (pile yarns) and 40% (ground yarns) virgin PVA mass adds based on the original slashing PVA mass into the

final recycled T-66 PVA size formulations achieved the required slashed yarn properties for effective terry towel weaving.

- The bending length of the recycled T-66 PVA slashed pile yarn decreased with recycling number, facilitating loop formation on the terry towel loom. Similarly, the bending length of the slashed ground yarn also decreased with recycling number. The decreased bending lengths of the recycled T-66 PVA slashed pile yarns provide an additional incentive for towel manufacturers currently operating on PVA/starch blend sizes with no recycle to convert to VFE recovery and recycle of all-PVA size formulations.
- Desized yarn CIE ΔL, Δa and Δb values remain constant with recycling. Overall color difference, ΔE, values were near one, which confirmed the visual conclusion that the desized yarn color build-up with recycle number was difficult to differentiate by the human eye. The minor color developed in the desized yarns should not interfere with dyeing pastel shades on the subsequent woven towels, even if it is not completely removed in the preparation processes that normally follow desizing (scouring and bleaching).
- Diffusion of the recycled T-66 PVA size across the yarn cross-sections increased with recycling number, but the desizing efficiencies remained constant (~99%). This trait is important for further wet processing of the desized towels, e.g., dyeing, printing and finishing (Section 2.1.3).

- The technical feasibility of implementing the VFE technology for PVA recovery and recycling was proven.

Based on the economic studies, the following conclusions were drawn:

- The overall cost savings of incorporating the VFE all-PVA concentration technology into a commercial-scale, conventional model towel manufacturing plant (143,700 lbs/day production, generating 100,000 gal/day of 1% solids concentration desize effluent stream) over the same model plant operating on a PVA/starch (60/40) size blend platform with no recycle was ~$3.2M/year.
- The VFE implementation savings were only slightly affected with increases in energy prices, i.e, for model plant on increasing natural gas price from $10/MBtu to $20/MBtu projected saving increase $0.2M/ year.
- The raw return on capital investment (R0I) period for VFE incorporation in the model plant was less than one year, based on an ~$3M total capital investment cost for the model plant provided by VACOM, LLC (Section 5.7).

CHAPTER 7

RECOMMENDATIONS

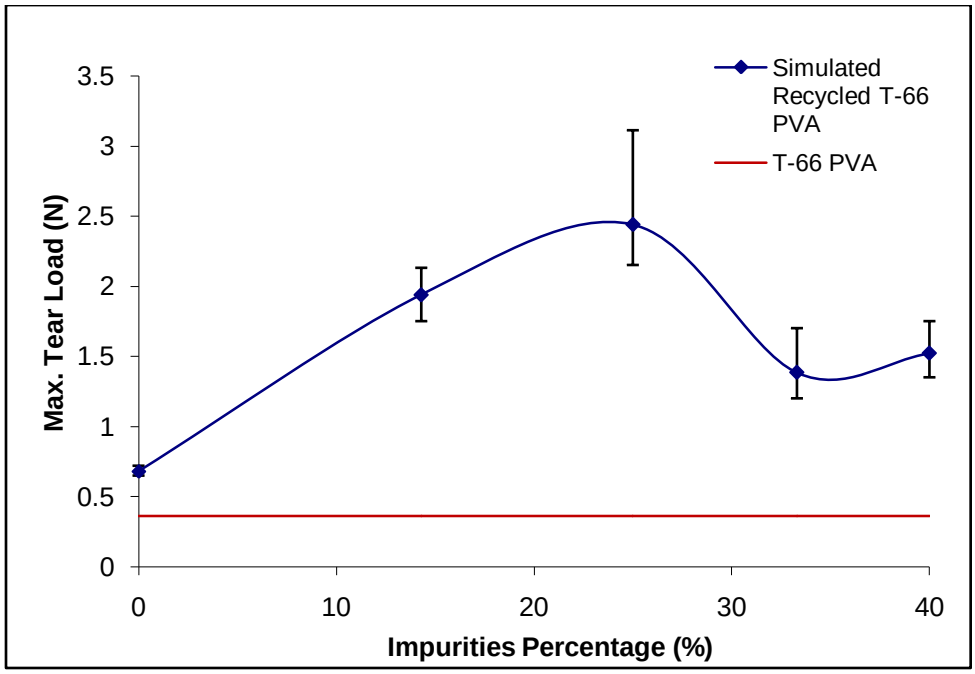
The reported research confirmed the technical and economic viabilities of the VFE process for PVA size recovery and reuse at a pilot scale. To transfer the research into commercial practice, the research results should be first translated to long-term, industrial-scale plant trials.

Industrial trials should be conducted using a large (10,000 gal/day of desize effluent stream capacity) pilot scale VACOM, LLC VFE unit, an appropriate number of terry towel looms for comparative weaving efficiency studies, an industrial slasher and a segregated desizing line. Initially, first weaving cycle towels should be produced by using ground and pile yarns slashed by the E. I. DuPont recommended all T-66 PVA/wax slashing formulation (93/7). For subsequent slashing cycles and after desizing the first (conventional) cycle towels, the VFE concentrated PVA size supplemented with virgin PVA adds at the proscribed levels for pile (20% of original PVA) and ground (40%) yarns should be used for subsequent slashing cycles. The resulting woven towels should be made from recycled size slashed yarns while monitoring weaving efficiency, and the products should then be desized separately so that PVA can be recovered via the VFE unit from the desized effluent stream. Six total cycles (one conventional and five size recovery and reuse) should be conducted in a sequence, and the results should be compared to those generated in the reported research. If the results of the plant trials parallel those reported in the research, then the slashing sequence should be extended to 12, 18 and 24 total sequences, with yarn properties and weaving efficiencies monitored

and compared with the initial (conventional) slashing at every step. Finally, a detailed economic study should be conducted comparing the operational costs of the overall VFA all-PVA size recovery and reuse process with the plant's existing PVA/starch size blend process with no size recycling, and a decision reached on full plant implementation of the VFE technology.

APPENDIX 1

TEARING BEHAVIOUR OF SIZE FILM



Maximum Tear Load Exerted by Simulated Recycled T-66 PVA Size Film vs. Impurities Percentage

APPENDIX 2

IMPURITIES PERCENTAGE CALCULATION IN PILE AND GROUND SIZE FORMULATION

Add-On on Ground Yarn %	G	10
Add-On on Pile Yarn %	P	3
Ratio of Pile to Ground Yarn P/G	L	6
Ratio of Filling to Ground Yarn F/G	M	1
Impurity % in Pile Yarn	x	2.1
Impurity % in Ground Yarn	y	2.1
Impurity % in Filling Yarn	z	2.1
Virgin % in Pile	A	20
virgin % in Ground	B	40
Size left in the yarn	Q	5
Total Yarn (1+L+M)	T	8

$$N1 = \frac{P * L}{T * 100}$$

$$N2 = \frac{G}{T * 100}$$

$$N3 = N1 + N2$$

$$D = (100 - Q) * \frac{N3}{100}$$

$$N6 = \frac{x * L}{T * 100}$$

$$N7 = \frac{y}{T * 100}$$

$$N8 = \frac{(z * M)}{T * 100}$$

$$E = N6 + N7 + N8$$

$$F = D + E$$

Size Add-On on Pile	N1	0.0225
Size Add-On on Ground	N2	0.0125

Total Size Add-On	N3	0.035
Size Desize	D	0.03325
Imp. From Pile	N6	0.01575
Imp. From Ground	N7	0.002625
Imp. From Filling	N8	0.002625
Total Imp	E	0.021
Total Solid After Desizing	F	0.05425

$$S1 = \frac{P * L * (100 - A)}{100{,}00 * T}$$

$$S2 = \frac{G * (100 - B)}{100{,}00 * T}$$

Recycle Size in Pile	S1	0.018
Recycle Size in Ground	S2	0.0075

$$An = (100 - Q) * \frac{Ip(n-1) + Ig(n-1)}{100} + E$$

$$\text{Impurities in Pile Size Formulation} = Ipn = \frac{S1 * An}{F}$$

$$\text{Impurities in Ground Size Formulation} = Ign = \frac{S2 * An}{F}$$

$$Ipn\ \% = Ipn * \frac{100}{N1}$$

$$Ign\ \% = Ign * \frac{100}{N2}$$

APPENDIX 3

COTTON CHEMICAL IMPURITIES CALCULATIONS

Percentage of Pure T-66 Left at 650 ^{o}C: Ta%

Percentage Pure of Cotton Impurities Left at 650 ^{o}C: Ca%

Percentage of Desized Solid Left at 650 ^{o}C: Da%

Desized Solid Compositions are Pure T-66 and Pure Cotton Impurities.

If a sample of 100 gm. Desized Solid have A gm of Pure Cotton Impurities than

Percentage of Pure T-66 is (100-A) gm.

Cotton Impurities Left in the Desize Solid at 650 ^{o}C: $A * \frac{Ca}{100}$ (1)

T-66 Left in the Desized Solid at 650 ^{o}C: $(100 - A) * \frac{Ta}{100}$ (2)

So Desized Solid Left at 650 ^{o}C: $Da = A * \frac{Ca}{100} + (100 - A) * \frac{Ta}{100}$

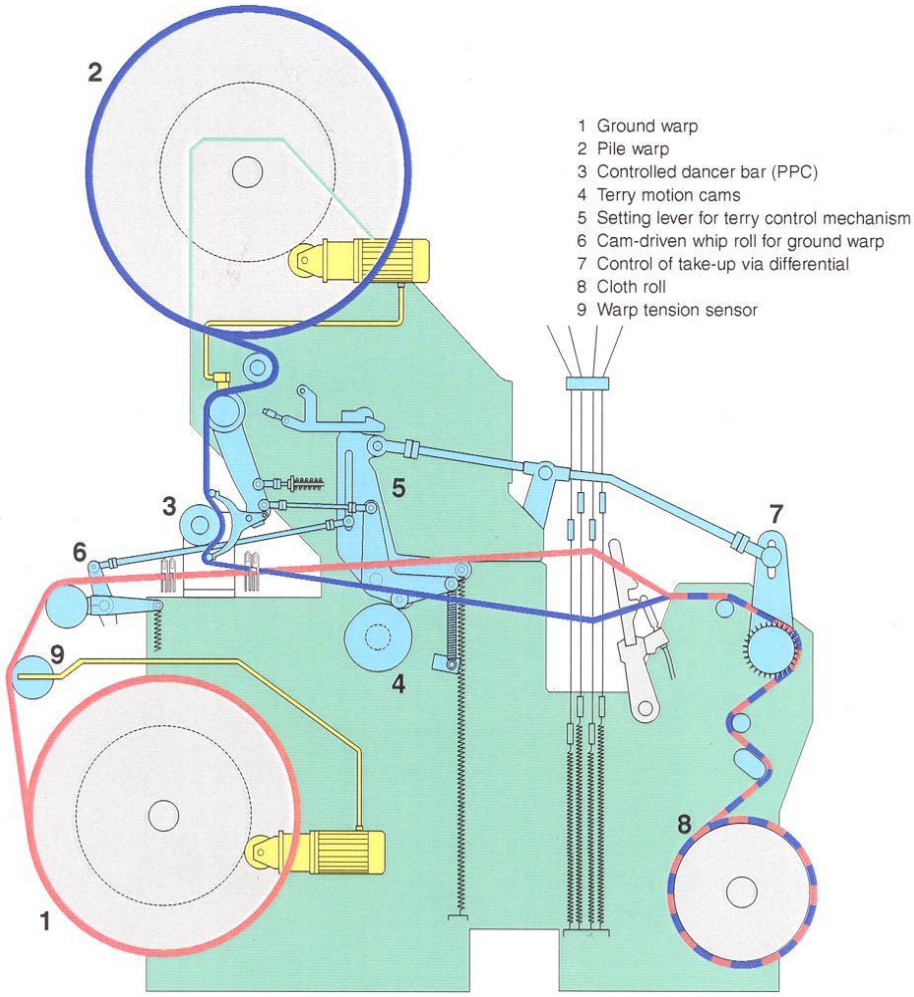
On Simplifying:

$$A\% = \frac{(Da - Ta)}{(Ca - Ta)} * 100$$

$$Impurity\ \% = \frac{(Ash\ \%\ in\ the\ Sample - Ash\ \%\ in\ the\ Elvanol\ T66)}{(Ash\ \%\ in\ the\ Cotton\ Impurity - Ash\ \%\ in\ the\ Elvanol\ T66)} * 100$$

APPENDIX 4

TERRY LOOM, SIDE VIEW



(Source: PTFE 3720 Class Slides, Spring 2009)

APPENDIX 5

ECONOMIC VIABILITY OF VFE PROCESS

	VFE (PVA/Wax)	Without Recycling (PVA/Starch/Wax)
Towel Production/Day (lbs) (Towel Construction Ground:Pile:Filling::1:6:1)[28]	143,700	143,700
Size Used in Pile Yarns (lbs) All-PVA/Wax Slashing Pile Add-Ons 3%, Conventional-PVA/Starch/Wax Slashing Pile Add-Ons 7% [28, 70]	3,233	7,544
Size Used in Ground Yarns (lbs) All-PVA/Wax Slashing Ground Add-Ons 10%, Conventional-PVA/Starch/Wax Slashing Ground Add-Ons 20%	1,796	3,592
Impurities Extracted in Desizing (lbs)	3,305	3,305
Total Solids in Desize Effluents (lbs)	8,334	14,441
<u>OPERATING COSTS OF PVA RECOVERY/REUSE SYSTEM</u>		

Desize Effluents/Day (Gallons)	100,000	175,000
Plant Costs (Capacity 100,000 gallons/day)[1]	$ 3,000,000	$ 0
Energy/ Gallon (MBtu)[1]	0.000595	$ 0
Energy/ Day (MBtu)	59.5	$ 0
Energy Price/MBtu (Natural Gas)	$ 10	$ 0
Energy Costs/Day	$ 595	$ 0
Labor/Gallon (VFE: 1 operator per 12-hour shift. Operators Salary =2* ~$65,000/yr, Benefits =2* ~$17,550)[1]	$ 0.0045	$ 0
Labor/Day	$ 450	$ 0
Maintenance Costs /Gallon [1]	$ 0.0036	$ 0
Maintenance Costs /Day	$ 360	$ 0
Total Operation Costs/Day (Energy, Labor, Maintenance)	$ 1,405	$ 0

SAVINGS FROM PVA RECOVERY/REUSE		
Water Recovery	~100%	$ 0
Desize Solids Recovery	100%	$ 0
Desize Solids Recover/ Day	8,337	$ 0
Savings from Size Recovery/Day T-66 PVA ~$1/lb	$ 8,337	$ 0
Wax Mass Savings/ Day (In VFE Recycled Size wax was not used, otherwise Wax used 8% of PVA) lbs	666	$ 0
Savings from Wax Deletion/Day ($0.60/lb)[72]	$ 400	$ 0
Savings from Water/Day ($2/1000 Gallons)	200	$ 0
Energy Used in Heating Water from 16^{o}C to 90^{o}C (MBtu)	110	$ 0
Savings from Energy Used in Heating Water/Day ($10/MBtu)	$ 1,100	$ 0
Savings from Waste Water Treatment/Day ($4/1000 Gallons)	$ 400	$ 0
Total Savings (Water, Size, Wax, Heating Water and Waste Water Treatment)	$ 10,670	$ 0

Net Savings/Day (Total Savings/Day - Total Operation Costs/Day)	$ 9,265	$ 0
Net Savings/Year (350 Working Days/Year)	$ 3,161,178	$ 0
Need for POTW for Desize Effluent Stream?	No	Yes

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